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**Fire Protection Research For Energy Technology
Projects; FY 79 Year-end Report**

January 1981

Prepared for

**United States Department of Energy
Assistant Secretary for Environment Office of
Compliance and Over-view
Division of Operational and Environmental Safety
Washington, D.C. 20545
Under Contract No. W-7405-ENG-48**

Prepared by

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Projects; FY 79 Year-end Report***

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and D.G. Beason**

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SUMMARY

This report describes work performed in fiscal year 1979, on a DOE funded study entitled "Fire Protection Research For Energy Technology Projects." The primary goal of this program is to ensure that fire protection measures for Fusion Energy Experiments (FEE) evolve concurrently with the complexity of FEE. Ultimately, it is planned that the detailed study of fusion experiments will provide an analytical methodology which can be applied to the full range of energy technology projects.

We attempt to achieve this objective by coordinately advancing 3 (three) major task areas; (a) determine the fire hazards of current FEE facilities (b) assess the ability of accepted fire management strategies to meet and negate the hazard, (c) perform unique research into problem areas we have identified to provide input into analytical fire growth and damage assessment models.

Through detailed study of the 2XIIB magnetic fusion facility and the Shiva laser fusion facility at LLNL, we have obtained a good engineering description of the state of the art of fusion fire protection. We applied fault tree analysis to assess fault modes in the fire protection systems. Concurrently, we continue to develop analytical techniques for assessing the fire hazards of these facilities.

Furthermore, we have conducted general surveys, outside of LLNL, of several European and two domestic fusion facilities.

To support our fire growth and hazard analyses, preliminary techniques for physical and chemical aerosol analyses have been developed and implemented. In addition, preliminary measurements of the dynamics of cable fires in our small scale apparatus have been completed.

Finally, with the aid of Econ, Inc., we have drafted a loss assessment protocol which is the ultimate output of this study.

*This work was performed under the auspices of the U. S. Department of Energy by Lawrence Livermore Laboratory under contract No. W-7405-ENG-48.

OVERALL LOSS ASSESSMENT METHODOLOGY

Although this study is primarily tailored to aid the Department of Energy in its decision making processes, the results and recommendations from the completed fire loss assessment for each of these facilities should also provide guidance for:

- o Managers of DOE supported national laboratories.
- o Experimental program managers.
- o Fire protection engineers.
- o Plant engineers and architects.

It is necessary to address both the federal level and individual laboratory level because large scale-costly fires in fusion facilities will have a distinctly different effect at each level. From DOE's standpoint a long term delay in key fusion research facilities could drastically prolong long term energy plans. On the other hand, individual laboratories are required to adhere to strict time lines and budget constraints in order to remain competitive in the fusion race. A long and/or costly interruption in their research due to fire could mean a loss of technological advantage over other labs or, if drastic enough, termination of the program. In many cases, fusion research constitutes a large percentage of funding for individual national laboratories, and termination of one of these programs would have a pronounced effect on the economic well being of the entire laboratory.

So that the magnitude of risk and consequence is appreciated by all concerned, our study will ultimately provide primary alternatives and recommendations of hazard mitigation for each level of management. Primarily, our study will define the potential hazard and damage of the resultant fire in each facility. Concurrently, the reliability and capability of the fire protection system to cope with such a fire threat will be assessed. Deficiencies or problems in terms of unacceptable reliability, inadequate effectiveness of the FPS will be identified from this match and the resultant risk would be identified and evaluated for critical spaces. We will attempt to present the majority of factors comprising this risk in monetary terms and, also the effect of alternative solutions in reducing this risk. Ideally, then,

decision makers will be able to determine an acceptable level of safety commensurate with their objectives.

SUMMARY OF PROGRAM METHODOLOGY

As cited in previous reports ^{1,2} we have been analyzing both the 2XIIB magnetic fusion and the Shiva laser fusion experiments. We are performing detailed studies on them so that they may serve as models for assessing the fire safety of all DOE supported fusion facilities. It is fortunate that the 2XIIB and Shiva are housed in structures which represent opposite ends of the spectrum (fig. 1 illustrates these differences). The 2XIIB resides in a building designed for previous applications, and is protected by an existing fire protection system. This does not mean that the system is inadequate for the experiment but rather that it evolved as the need for greater fire protection was recognized. Shiva, on the other hand, has contemporary fire protection systems. Its design was included in the construction package of the experiment. Most facilities will have fire protection systems that tend toward either end of the range or fall somewhere in between. Therefore, we should be able to apply the methodology developed for 2XIIB and Shiva to all fusion facilities.

Figure 2 is a general schematic of the protocol we have been using in our analyses. Currently, however, we have only been able to progress down to the third step in the sequence. For the 2XIIB and Shiva facilities we did the following:

1. Divide the building into zones based on the separations provided by walls and also the content and function of the space. Identify "critical" zones which would have great economic and/or programmatic impact on the research facility if damaged.
2. Analyze selected zones for fire impact. A flowchart of the logic to define fire impact is shown in Fig. 3. The schematic shows that assessment of fire impact depends on analyzing the fire hazard and the response of the fire protection system. Fire damage and resultant loss will be modified by reaction time and effectiveness of fire countermeasures. For the 2XIIB

enclosure we analyzed inherent fire hazards using techniques that consider probability of ignition rate of flame spread, and heat release potential of construction materials, electrical and thermal insulations, and dielectric fluids. Results of this study were incorporated into a fire growth analysis based on large-scale fire test data and exponentially increasing heat release rates derived from several existing fire growth models. The analysis maps development of the fire with time and the status of fire protection system.

Concurrently, we used qualitative and quantitative fault tree analysis to assess system design, system hardware, and maintenance policies. The results indicate availability and reliability of the system on demand.

For Shiva we have applied a general qualitative fire hazard analysis identifying potential fuel sources found in selected areas. The reason for this limited analysis is that we are seeking a more effective fire growth modelling technique to augment this study. However, we have obtained good descriptions of Shiva's overall fire protection strategy, and component parts of the overall system.

SHIVA ENCLOSURE

The plan and transverse section for the Shiva experiment are shown in Figs. 4 & 5. Passive fire protection for building 391 is provided in the form of fire rated barriers and components in a building composed largely of concrete and structural steel.

To make our study manageable, we chose four critical areas of the building to evaluate. These spaces were the; laser bay (Rm. 1330), target room (B-306), control/diagnostics room (1210) and energy storage area #1 (B-329). Table 1 summarizes pertinent characteristics of these rooms. The table indicates factors, other than high loss potential, which were of concern such as; extreme ceiling heights, lack of barriers (continuous volumes), and areas with high ignition probabilities which communicate with critical spaces (energy storage area #1).

Extreme ceiling heights in the laser bay and target room can result in maximum automatic fire detection and suppression response times. Also, large

continuous volumes will allow fire to develop unhindered for substantial time periods. In contrast, the control/diagnostics room has a 3.05m(10') ceiling height and is of fairly conventional volume. But, crucial here is that even small fires could cause harm to critical components necessary for performance of the experiments. Moreover, energy storage area #1 in the basement of building 391 contains a large number of oil filled capacitors which have documented potential for failing and igniting adjacent materials; e.g., large diameter power cables, electrical insulation and dielectric spacers. The cables interconnect capacitors and penetrate the first floor slab to power the multiple laser "arms" of Shiva. Consequently, a fire originating in the energy storage area could spread to the laser bay or, possibly worse, corrosive combustion gases could be transported through the floor penetrations and cause damage to fragile laser components and instrumentation.

FUEL LOAD AND VENTILATION SURVEYS

Table 2 qualitatively describes potential fuels and fuel distribution in each critical area of Shiva. Fuel quantities in large bays are concentrated in widely distributed groupings. These are typically bundles of power, diagnostic, or signal wire. However, the control/diagnostics room, by its nature, has much higher fuel loading, relative to its volume. Generally, these fuels are ordinary combustibles such as computer printout, and a variety of plastics (mag tapes, discs, etc.).

Table 3 is a summary of the total amount of air available from both ambient and mechanical sources for both natural and mechanical, for the four areas studied.

Because a detailed quantitative fuel load study has not yet been carried out, the cellulose and polyvinylchloride (PVC) columns are included to give a relative idea of the total amount of these materials which could theoretically burn with the available air excluding the mechanical ventilation. The necessity for having large volumes in the main experimental areas provides an abundance of air to support a great deal of combustion.

As in 2XIIB, LLNL records show that most ignitions in Shiva have been small and were caused by welder's torches or electronic components that shorted, overloaded or exploded. All these ignitions were detected quickly and caused only very minor damage.

FIRE DETECTION SYSTEMS

The fire detection system is part of a general protective signalling system consisting principally of a hardwired circuit with detection devices on one end and an emergency control console on the other. This dispatcher attended console monitors all fire emergency circuits such as smoke detectors, tamper switches, personnel calling by phone, etc. Specifically, fire detection is accomplished through one or more of three primary modes in each zone or compartment in the Shiva facility. The first mode is automatic detection which relies on products of combustion detectors of one type or another located throughout the building. Ceiling mounted ionization type detectors are located in the majority of the building with the exception of the Laser bay, Target room, and clean room areas which are monitored by an "Incipient Fire Detection (IFD) System". The following is taken from the Environment One Incipient Fire Detector brochure;

"The IFD system operates on the Wilson Cloud chamber principle which allows the invisible particles produced at the incipient^{*} state of fire to be easily detected by optical technique. The IFD is an active, self-monitoring system. Because particles are always present in low concentration, it must sense the particle concentration once each second and failure to do so will activate a malfunction signal. Any increase in the concentration to a preset threshold level generates an electrical signal which activates an alarm relay."

The sampling heads for the IFD system pull from the ventilation exhaust ducts in each zone once every 15 seconds. The second mode, manual detection requires building occupants to pull a wall mounted fire alarm box or call on the telephone.

Lastly, fire detection or rather fire alarm is keyed to sprinkler system activation. Flow switches are placed adjacent to each zone OS & Y^{*} valve to monitor flow to each zone. Therefore, although response would be much slower, if for some reason the other two modes failed to pickup fire signs, the activation of the sprinkler system acts as a backup alarm device. Obviously, another function of monitoring the sprinkler system is to signal occupants and

^{*} Outside screw and yoke.

the fire department of an accidental release of the system. The three detection modes are present during regular working hours.

However, during the evening when the building is sparsely populated only two automatic modes of detection are operational.

DESCRIPTION OF SHIVA FIRE SUPPRESSION SYSTEM

Fire protection for the Shiva experimental facility is provided through both active and passive systems. Although sound fire protection design integrates these two elements, our study will reference the building's passive fire protection characteristics only as they impact the performance of the active system.

Figure 6, is a block logic diagram of the system which consists primarily of a wet-pipe sprinkler system and a combination of automatic and manual detection capabilities. In areas where additional or specialized protection is needed, other fire protection components are provided, as shown in Table 4. Specifically, a Halon 1301 system is present below the control/diagnostics room (1210) floor and a high expansion foam system resides in the target room with a sprinkler system under the floor. Along with these systems, the heating, ventilation and air conditioning (HVAC) is designed to shut down (triggered by the incipient detection system) in the event of a fire in the laser bay, target bay, and clean room (see Table 4 and Fig. 6). The reason for this action is that ceiling to floor air flow of the ventilation system would greatly increase the activation time of the sprinklers by inhibiting the connection of hot combustion gases to the fusible links.

WET PIPE SPRINKLER SYSTEM

The primary fire protection system for Bldg. 391 is a wetpipe sprinkler system, hydraulically designed to reach each major building compartment through one of two sprinkler supply risers. Each riser, located in the northwest and southwest-corner of the building, supplies independent sprinkler systems. The north riser supplies the sprinkler system for the majority of the basement. The south riser provides water to energy storage area no 2, the

electrical/mechanical room, receiving room, control/diagnostic, laser bay, target room, and the balance of the building.

Sprinkler head (standard 165°F fusible link type) distribution is uniformly spaced at approximately eight to eleven feet, depending on the zone. Spacing of branch lines varies up to a maximum of forty feet apart in energy storage area no. 1 below the laser bay. The dedicated water supply system is more than adequate, but in case of a break in this main water supply, reserve water capacity and pressure for both risers requires the hookup of an LLNL Fire Department pumper truck, its crew, and a reliable backup water source.

PRELIMINARY ANALYSIS OF SHIVA FIRE PROTECTION STRATEGY

The following analysis of the Shiva (Bldg. 391) fire protection strategy is an expansion of that performed for the preaction system in the 2XIIB facility. The analytical technique for Bldg. 391 is the same as that for the 2XIIB, except that Shiva has a contemporary, multi-faceted fire protection system which was evaluated as a whole and, currently, some of its component parts. Again, the technique involves both qualitative and quantitative evaluation for the probability for failure assuming a fire exists. Also, a preliminary evaluation was made of the probability of "accidental sprinkler release."

Fault tree analysis was used to qualitatively and, for selected components, quantitatively analyze the reliability/availability of:

1. the overall fire protection system,
2. the wetpipe sprinkler system,
3. Halon 1301 system,
4. Incipient detector system,
5. Fire Indicating Unit and Zone Indicating Unit (FIU/ZIU).

System availability was calculated for the Laser Bay, Target room, Energy Storage Area #1, and the Control/Diagnostics Room. As mentioned previously these areas were chosen because they represent "critical"* areas in the facility. For example, if the control room were to suffer major damage, the experiment would be disabled for a costly period of time. Furthermore all the

* Preliminary assessment of criticality performed by the Fire Science Group.

fire protection control panels, their emergency power supply, etc. are housed in the control room. Thus, access to these critical controls would be denied to firefighters.

The basic steps followed to analyze the Shiva Fire Protection System (FPS) were as follows:

- a. Identify all components in the FPS, both automatic and manual.
- b. Construct a logical block diagram delineating the structure, interconnections, and dependency of components.
- c. Perform "top level" fault tree analyses of the system to identify critical components and failure modes.
- d. Perform detailed qualitative and/or quantitative analyses on identified critical components.

Relative component and system reliability figures are partially available for those areas under study. Existing reliability data for both analyses were drawn from the following sources:

National Fire Protection Association
LLNL Maintenance crews
LLNL Fire Department personnel
Facility P & IE Drawings
IEEE Standard 503
United Kingdom Atomic Energy Agency
Factory Mutual Research Corp.

A crucial step in the analysis of Shiva's fire management system is an accurate understanding and resultant description of the relationship between the detection and response circuits. This is obtained by showing the interrelationship of each component system in the block diagram. Fig. 6 resulted from this process. It delineates those areas or zones which have additional specialized detection and/or suppression devices (e.g. Halon 1301, high expansion foam) and, it shows the path of components which must activate in the event of a fire. By tracing this path we perceive the type and number of components which can potentially fail, during operational demand. From the diagram we note that both manual and automatic detection systems must pass through the fire/zone indicating units (FIU, ZIU). These units relay any

trouble or emergency signal directly to the fire department 24 hour dispatch unit. They also supply power to most automatic detection units. Failure of the FIU and/or ZIU would prevent emergency signals from reaching the fire department, constituting a common mode failure in the overall fire detection scheme for the facility.

On the response side, we can see that the wet-pipe sprinkler system which is the primary automatic suppression device for the building is completely independent of the FIU/ZIU. Consequently, failure modes for the sprinklers involve only components within the sprinkler system (e.g. heads, piping, and valving).

The Halon 1301 system under the control room floor requires the keying of 2 smoke detectors, one from each cross zone before it will release suppressant. However, a local alarm will sound before actual Halon release which provides a short period of time to manually override the system.

During daytime hours the experiment is normally occupied by experimental personnel who provide a third mode of detection and possibly suppression. As human detectors, probably their most valuable function is to signal alarm by either pulling a manual fire alarm box or by calling the fire department on the phone.

Testing and maintenance procedures consist of checking flow to each zone twice every quarter. This task is accomplished by opening a drain valve in the vicinity of the OS & Y gate valve for the zone. Since the drain valve is downstream, this procedure guarantees that the OS & Y's are open. Typically, these valves are locked in position via padlocked chains. However, no check is made for flow internal to a zone. Flow restrictions due to corrosion, sediment, and foreign substances downstream of the test drain are not typically covered by this procedure.

In this analysis, we assumed the following:

- o Components, subsystems, and similar items can have only two conditional modes; they can either operate successfully or they can fail. No operation is partially successful.

Basic failures are independent of each other.

- o A component in the fire protection system can fail in four ways when there is a demand.
 - (1) It can fail to change state, for example, relay contacts fuse closed.
 - (2) It can fail and failure can go undetected (no repair), e.g., a plug in the pipe line. (Failure probability, $P = \lambda \tau$, where λ = failure rate, $P = 1 - e^{-\lambda \tau}$, where λ = failure rate.)
 - (3) It can fail and failure can be detected; i.e., the component is under repair (announced failure). For example, a sprinkler head leak is detected by the flow switch. ($P = \lambda \tau$, where τ = repair time and λ = failure rate.)
 - (4) It can fail and failure can be detected at the end of scheduled inspection; i.e., the component is under repair (unannounced failure). For example, the OS & Y valve is shut off and the tamper switch fails. Two failures are detected at the next inspection. ($P = \theta/2$, where θ = the inspection interval.)

Success in predicting the probability of a specific occurrence depends on how accurately the system is represented in a fault tree, how detailed the tree is, and how valid one's mathematical expression and probabilities are. Table 5 summarizes the results of both qualitative and quantitative analyses of the four critical spaces. The qualitative analysis which was supported by the FTAP³ computer code, requires no numerical or probabilistic data input. Results of this analysis provide insight into the logical structure, design, and maintenance of the fire management system in relation to scenarios for system failure. The quantitative analysis, which was performed through the use of the computer code IMPORTANCE⁴, estimates system failure probability (vulnerability) by quantifying and ranking potential system failure modes. This is accomplished by the logical manipulation of component failure rates.

In Table 5 the quantitative values show an overall failure probability of fire protection systems in each space; more specifically, the numerical magnitude represents the probability that at least one of the automatic detection devices will react to a fire. Only the automatic devices were considered in the analyses because we felt that critical time for a fire to occur would be in the evening when the building is sparsely populated. This perception is reflected in the two columns entitled "Minimum Failures of Subsystems," which

lists minimum potential failure modes for both daytime and night operation; the absence of occupants accounts for the reduction in redundancy from 3 to 2.

Note that the availability (1-unavailability) figures are high (98.7 - 99.5%) in all spaces. High probability of success can be attributed to redundancy of fire protection in these spaces. The probability of all systems failing simultaneously is very low. Because the sprinklers are independent of the other systems they are essentially eliminated as potential common mode failure points in these spaces.

Table 6 summarizes the results of the analyses of the different fire protection elements in the Shiva building. Current, quantitative availability data were generated only for the FIU/ZIU unit and the wetpipe sprinkler system. The evaluation of the remaining components has been limited to a qualitative look, primarily due to the lack of applicable failure data and also restriction of available time.

Detailed breakdowns for the minimal cutsets has not yet been completed, but the range of these sets based on the number of basic events contained for each subsystem has been listed. For example, the range for the Halon 1301 system of 1 to 8 means that it had min cutsets containing up to a maximum of 8 failure events and a minimum of 1 event to compromise the system. Notice the high availability of the FIU/ZIU units which are the potential common mode failure points for a majority of the detection measures. However, these units contain a large number of possible single point failures, any one of which could cause the units to fail; preventing the operation of several detection subsystems.

The wetpipe sprinkler system has a high availability probability, which is logical considering the components that comprise the system. Basically, these elements are piping, joints, sprinkler heads, and valving which all have low probabilities of failure. As in the previous analysis (2XII B facility)^{1/2} a model of the sprinkler system was used consisting of a square grid with a sprinkler head at each of the four corners. Failure of the system requires the failure of all four sprinkler heads in response to a fire.

A detailed description of the preaction sprinkler system in the 2XIIB facility was presented previously in references 1 and 2. Figure 7 illustrates the components and logic specific to drypipe preaction systems and wetpipe systems. The diagrams indicate that the preaction system in 2XIIB is more complex than the wetpipe system. Thus we would expect wetpipe systems to be more reliable than drypipe systems, so long as; maintenance periods, skill of maintenance personnel, and availability of water are equal.

To fail Shiva's wetpipe system one of the following must occur;

- o Failure of 4 out of 4 sprinkler heads.
- o failure of piping
- o failure of valving

However, in addition to the above wetpipe failure modes, the drypipe preaction system is subject to failures of:

- o smoke detectors
- o pressure switches
- o and the FIU/ZIU electrical supervisory circuit.

All of which contributed significantly to drypipe sprinkler system failure. Conversely, we would expect that the wetpipe sprinkler system brings with it a higher probability of accidental release.

QUANTITATIVE RESULTS

Probability of sprinklers system failure (to activate as required) was calculated on a per demand basis over a fifteen year period. Probability of inadvertant water release was estimated on a per year basis. Results of the two analyses indicates probability of success for the two systems:

<u>System Type</u>	<u>Probability Estimates</u>	
	<u>Ability to Operate When Required</u>	<u>Accidental Release</u>
Wet Pipe Sprinkler System (Shiva)	98%	10^{-5}
Drypipe/Preaction System (2XIIB)	82%	10^{-5}

The addition of the FIU/ZIU circuit and the detectors provides a substantial decrease in the probability of an accidental release. However, the direct consequence of adding these components is an increase in failure modes and, therefore, a much lower probability of success per demand (82% V.S. 98%).

To varify our results, we collected "successful operation" of sprinkler system statistics accumulated in the commercial sector by comparing data from:

- o National Fire Protection Association
- o Factory Mutual
- o Australia
- o United King

This comparison is shown in Table 7, which indicates that our analytical results are well within the range of actual historical experience. Of course, as in any body of statistics, we must use caution in interpreting what "satisfactory performance" means from each data source. The Australian data, which includes extinguishment by all means is a prime example at 99.8% satisfactory performance. Nevertheless, in rough terms the fault tree results agree very well with the existing statistics. Furthermore, our calculated estimate of (10^{-5}) for accidental water release was within an order of

magnitude of ten years of the Factory Mutual System loss data⁵ for an estimated 48 million sprinklers. These historical statistics from 1967-1976 which covered premature operation due to all causes (i.e., overheating, freezing, mechanical injury, corrosion, excess pressure, etc.) yielded a probability of release of 1.6×10^{-6} . It appears that premature release of water, even for a wetpipe system, is a very low probability event. Since the preaction system is designed to prevent accidental releases, its probability is even lower than a traditional wetpipe. However, the trade-off with regards to system operation upon demand is not worth the minimal increase in safety from accidental releases.

SURVEYS ON NON-LLNL FUSION FACILITIES

Currently, work is continuing on a detailed survey protocol for off site fusion facilities. However, the following outline describes our preliminary analysis (using our preliminary survey protocol) of facilities that members of the Fire Science Group visited in the past year.⁶

A. SANDIA EBFF

Fire Hazard: Marx generators, capacitors, large quantities of cable insulation and dielectric fluid in open reservoir, frequent fluid transfer, boiler room close to dielectric reservoir and fire main.

Ventilation: HVAC.

Detection/Suppression: Smoke detectors in screen room, central water-flow alarm, wet-pipe system for large fires reliability of 95%/demand, high bay 40 ft ceiling; small fire could cause damage before sprinkler alarm is activated.

Effectiveness: Aerosol explosion could remove wet-pipe system, unknown potential of low-intensity fire.

Modifiers: AFFF corrosion potential, maintenance errors (Marx generator service), weather factors could slow Fire Department response from Kirtland A.F.B..

B PRINCETON TFTR

Fire Hazard: High energies, thermal and cable insulation, electric arcs.

Ventilation: HVAC.

Detection/Suppression: Local and central alarm, preaction dry-pipe sprinklers, smoke detectors, freon type extinguishers in specific and sensitive areas, 10 min Fire Department response.

Reliability: Preaction sprinklers 85%/demand.

Effectiveness: Poor location of detectors and sprinkler heads could lead to large loss. Fire Department at Princeton Township is several miles away.

Modifiers: Weather/traffic could slow Fire Department.

C. MAX PLANK IPP: Tokamak and Stellerators, Iodine lasers.

Fire Hazards: Cable and thermal insulations, trash in storage areas.

Ventilation: HVAC.

Detection/Suppression: Local alarm, few hose hookups, 10-15 min Garshing Fire Department response. Modifiers: Late detection, traffic, weather. In plant fire brigade, safety personnel on site 24 hrs/day.

D. CEN-G TOKAMAK: Plasma studies.

Fire Hazards: Cable and thermal insulation.

Ventilation: Windows.

Detection/Suppression: Thermal detectors, dry chemicals on carts, five men on site.

Modifiers: Weather, multiple fires, late detection and inadequate suppression.

E. CULHAM MFE Site of Joint European Tokamak (JET):

Fire Hazards: Cable and thermal insulation and many experiments.

Ventilation: Melt-out windows.

Detection/Suppression: Eight-man patrol, minimal automatic detection, local alarm, manual standpipes.

Modifiers: Fire Department remote from site. Obscuration of fire site in large fusion experimental area. There appears to be minimal interaction between CULHAM and JET personnel.

This tabulation indicates that:

- o The combustible material load, and consequently the fire risk parameters, at early times are quite similar for all systems (E-beam open oil reservoirs excepted).
- o European fire protection systems rely primarily on early warning from fire detectors and human interaction rather than automatic extinguishing systems.
- o Areas without dedicated fire-fighting personnel and equipment could suffer extensive property loss should the resident automatic extinguishing system fail.
- o The effect of unique features of experiments and experimental enclosures can be identified but not quantified at this stage of the analysis.
- o No human error modifiers are listed because of our inability to logically place such factors in our analysis.

CABLE EXPERIMENTS

Our fire hazard surveys have identified two generic cable jacket materials which represent the majority of those used for power transport in fusion experiments at LLNL; Polyvinyl chloride (PVC) and neoprene. The former is typically RG 220 A/U and the latter 4/0 welding cable. However, since the actual cables are 29 mm (1-1/8") and 19 mm (3/4") in diameter respectively, a smaller designation cable was used for the small-scale box experiments. For the RG 220 A/U, Times Wire RG 11 A/U was substituted and 6 AWG neoprene welding cable was substituted for the 4/0; both of these cables having an O.D. of around 10 mm (3/8"), (see cross sections, Fig. 8). These smaller size cables are identical to the actual ones, but their scale made them more valid for the fire exposure produced by the burner.

SMALL-SCALE CABLE FIRE EXPERIMENTS

In order to obtain necessary data for our fire growth analysis we performed small-scale fire experiments on representative power cables used in fusion facilities. The primary objective of this portion of the study is to obtain fire performance data which are not currently found in the literature or at other experimental labs. These primary fire performance characteristics include:

- o time to ignition
- o minimum ignition energy
- o rate of flamespread
- o total flamespread
- o burning rate (mass loss and O₂ consumption)
- o volume and density of combustion products
- o corrosive effects of combustion products.

The experiments described below are preliminary and exploratory tests to give us insights for the design of large-scale cable fire experiments. Ultimately, data from the large-scale tests will provide some of the essential factors for a predictive fire growth analysis for fusion facilities. In addition, we will attempt to correlate our small and large-scale results which, hopefully, will alleviate the need to perform an excessive number of large-scale tests.

DESCRIPTION OF EXPERIMENTAL SET-UP

The small-scale fire test facility shown in Fig. 9 has an overall volume of 0.42 m^3 (15 ft^3) and is equipped with 152 mm (6") diameter ventilation ducts that extend about 1.8 m (6') from both sides; air can either be forced or drawn through the box. The principle parameters which are monitored and recorded include airflow, optical density, enclosure pressure, fuel mass loss, temperatures, and flame radiation. Combustion gas samples are drawn from a point near the exhaust duct and their pH monitored (the Appendix). Figure 9 shows the location of the various sensing devices in and on the box along with the test specimen and gas burner. The pipe burner shown in Fig. 10 is 12.7 mm ($1/2$ ") diameter pipe with 1.6 mm ($1/16$ ") holes drilled on a 6.4 mm ($1/4$ ") grid. Its output is a premixed propane/air flame with an energy output of approximately 1530 J/S (90 BTU/min) which gives a total 5-minute run of 459 KJ.

BASELINE CALIBRATION RUNS

To determine the contribution of each type of cable to fire growth, the fire exposure produced by the burner alone was characterized via a number of calibration tests performed on a noncombustible cement asbestos board blank (Fig. 11). Radiometers to measure incident heat flux from the flame were placed near the base and top of the blank and also in the door of the box directly opposite the specimen. In addition, thermocouples were placed near each radiometer, at the center of the blank, and at locations throughout the box as shown previously. Protocol for this experimental series was to systematically run the burner at various gas/air ratios, monitor and record all data points, repeat, and select the fire exposure based on the following criteria:

- a) Incident radiant heat flux of flame.

We were looking for an incident heat flux from the flame of between three and four watts/cm². This choice was based on discussions with personnel from the National Bureau of Standards who recommend approximately three watts/cm² as the minimum ignition flux in their compartment tests. It is also a common range for other small-scale fire tests.

b) Flame height and area.

In order to determine the contribution to flame spread of the cable specimens the flame had to be sufficiently short. But it also had to have enough height and breadth to expose a fairly realistic area to ensure pyrolysis of combustible gases, etc.

c) Temperatures incident on the blank and air temperatures in the box.

We needed an ignition flame with a heat output that didn't mask the temperature contribution of the burning cable specimens.

d) Oxygen depletion.

A primary reason for specifying a premixed flame was to minimize the O_2 consumption in the box by the ignition source, which would allow us to monitor the oxygen consumption of the cable samples.

After performing a large number of these calibration runs we selected a baseline exposure flame with the following characteristics:

- a. Incident heat flux 3.25 watts/cm^2 ,
- b. flame temperature $500^\circ - 600^\circ\text{C}$,
- c. flame height 125 mm (5"),
- d. O_2 depletion - no effect,
- e. energy output 1530 J/S (90 BTU/min).

A composite plot of most of these parameters is shown in Fig. 12.

Figure 10 is a schematic of the specimen holder which, if completely filled, would contain a total surface area of 0.59 m^2 (91 in^2). However, to enhance flame spread, we left a one cable diameter space between each fuel element. This configuration accommodated 8-10 cables per sample which were restrained at both ends by the specimen holder.

To identify the contribution of each of the component parts of the PVC cable, we tested the individual parts as well as the entire cable. Therefore, at least three samples of each of the following cable specimens were tested:

- o PVC cable (whole)
- o Neoprene cable (whole)
- o PVC jacket alone
- o Polyethylene insulation with copper conductor

TEST PROCEDURE

Initially, fresh air is pulled through the box at a minimal rate and a scan of ambient conditions is taken. The burner is ignited, set to prescribed flowrates, and the specimen is exposed for a maximum time of five minutes. At predetermined times, the burner is shut off to ascertain if the cable continues to burn without the ignition flame. Figures 13 through 15 are examples of the data plots and a summary of results is presented in Table 8. Ignition exposures from 2-5 min were used to determine the minimum ignition time for the samples. Polyethylene sustains burning after a two-minute exposure while the complete PVC cable takes a four-minute exposure to sustain flame. The times to ignition were determined through visual observation and are, therefore, fairly subjective. The load cell to monitor dynamic mass loss lacked the sensitivity to pick up the very slight losses of the jacketing material. However, we were able to effectively measure the change in pH and oxygen depletion.

Results summarized in Table 8 show that PVC cable and jacket material rapidly produce acidic combustion products, whereas, burning neoprene insulated cable appears to produce fairly neutral gases (in terms of pH). We also tested the response of uncoated polyethylene dielectric for the PVC coated RG11 A/U cable. For times to sustained ignition, polyethylene dielectric required the least amount of time at 2:00 minutes; the PVC cable required 4:00 min of flame exposure, but, neither the PVC jacket material alone nor neoprene cable sustained burning after 5 min of exposure to the ignitor. The oxygen depletion data tends to substantiate the above showing low oxygen percentages for polyethylene and the PVC cable. Maximum temperatures at the mid-height of the sample and various locations in the box reinforce this to a lesser degree.

In summary, these preliminary measurements of the dynamics of cable fires have yielded the following conclusions:

- o PVC insulated cables produce large quantities of acid ion gases, and neoprene does not, under the conditions of these tests.
- o Acid ion gases from PVC has significant, demonstrated corrosive effect on sensitive computer electronics such as tape read/write heads. Also, aerosol adhesion to laser optics indicates severe cleaning problems and corrosion potential.
- o The polyethylene dielectric promotes the pyrolysis of the PVC jacket material.

(Note: A detailed report on the chemical analysis of the combustion gases from these experiences is included in the Appendix.)

ANALYSIS AND CONCLUSION

Although the small-scale box apparatus lacks sensitivity in a number of areas, it does differentiate trends in the fire performance of PVC cable, neoprene cable, PVC jacketing, and polyethylene insulation. As mentioned previously, the dynamic mass loss instrumentation could not accurately monitor the minute losses of the burning polymeric cable material. Similarly, times to ignition, light obscuration, rate of flame spread, and extent of flame were too similar to discriminate between the various samples.

However, distinguishable data were obtained for pH of combustion gases, time to sustained ignition, oxygen depletion, and temperatures in various locations in the box.

FUTURE WORK

Work in the next quarter has been initiated to corroborate, supplement, and expand the data acquired from the small-scale box experiments. We have contracted with SRI, International to perform a series of heat release rate (HRR) calorimeter tests on PVC and neoprene cables. In addition, we are presently validating an "Ease of Ignition" test apparatus which was developed

at the National Bureau of Standards. Presently, we are not aware of any existing data which gives the HRR of these cables in their composite form, nor is there information pertaining to relative ease of ignition. Both of these characteristics are very significant for determining the potential fire performance of various cable types and also as necessary inputs into our analytical fire growth methodology. This first-hand information will hopefully help us to accelerate our efforts in our fire growth predictions. Much of this experimental work should be completed in the next quarter.

CONCLUSIONS AND FUTURE WORK

Table 9 lists the overall program objectives for this project. Currently, we have used system safety techniques (primarily fault tree analysis) to define the state of the art of fire protection as applied to the fusion energy experiments we have studied to date (B). Moreover, we have been able to perform preliminary assessments of their fault modes (C). However, our analyses have not considered human error due to the complexity and difficulty in obtaining meaningful reliability data. It is unrealistic, considering the goals of this program, to attempt to quantify and include human factors into our evaluations and recommendations for fire protection since we primarily address in-place equipment and materials which DOE can effectively modify to improve the fire safety of its facilities. We have been quite encouraged by the agreement between data based on historical experience and our parametric analysis. It is a good indication that our analytical technique and reliability statistics are reasonable. More importantly, however, are the results which compare the availability of fire protection systems. i.e., because the operation of the dry-pipe preaction system is totally dependent on the FIU/ZIU circuits, its chance for failure upon demand is approximately ten times (2% V.S. 18%) that of the wetpipe system. Also, our calculated value of 10^{-5} per year for accidental sprinkler release from the dry pipe system as compared to 10^{-6} for industrial experience of wetpipe systems indicates that very little advantage is gained by sacrificing a factor of nine in reliability. This is the kind of information the DOE needs to make rational decisions on cost effective solutions in protecting their facilities.

In the next fiscal year, we will finalize the Shiva fire protection study and continue to refine the overall fire risk assessment methodology. This goal should be met through the continuation of the following tasks (Table 9).

D. Develop techniques for defining fire hazards of FEE.

We are currently working on more appropriate fire growth models for experimental fusion facilities. Contemporary fire growth analysis is primarily centered on residential fire problems. Our past efforts to apply promising theories to the large scale fusion energy experiments, results in a family of temporal fire growth parameters which vary by 100% in both time and intensity. This range of variability is unacceptable. Therefore, in the next fiscal year we will be studying other candidate analysis techniques which will hopefully yield a more accurate description of fire growth in these spaces.

E. Couple hazards analysis with fire protection systems analysis for LLNL facilities.

This phase of the program represents a very critical step in the overall program because it will ultimately predict the degree of damage for each of the facilities. In general terms, this task requires not only an accurate picture of the rate and extent of fire growth, but also the response of the fire protection system in terms of reliability and effectiveness. Logically, the amount of damage and the resultant loss will be dependent on the effectiveness and reliability of the fire countermeasures.

(F,G.) Develop survey protocol for FEE's at non-LLNL facilities and validate.

With the aid of Econ, Inc., we have been drafting a questionnaire, based on our studies here at LLNL, for off-site FEE's. From answers to the survey in its final form we should be able to perform an analysis of fire protection capabilities of these facilities utilizing the methodology we have developed through our studies here.

In FY'80 we will have a finalized version of the primary parts of this questionnaire and will begin to distribute it to selected FEE facilities.

H. Conduct research to solve identified problems.

Presently, we have completed preliminary small scale cable burns and obtained gross data points for common cable types found in LLNL fusion experiments. However, this effort was exploratory in context and conducted to give us an indication of what further research was necessary to give us the information necessary to refine our fire growth analysis. As mentioned previously, we will be conducting large scale heat release rate calorimeter tests at SRI, International on the cables we have identified, thus far, as representative FEE types in the next fiscal year. In addition, we will be performing "Ease of Ignition" tests on the same cables here at LLNL.

Since these tests will be performed on the cables in their composite form, a realistic set of data under each of the imposed test conditions should result. This information will help us understand more about the dynamics of cable fires. These data can be applied to: refine our fire growth analysis inputs as well as the rate of smoke aerosol production and the potential for corrosive attack on facility equipment.

In addition to these important inputs, chemical analysis of the combustion gases will continue for corrosive components. A complete report of the FY 79 effort in this area is included in the Appendix. This work will expand into the analysis of combustion products developed from the burning of other potential fuels common to fusion facilities, e.g. computer tape and cassettes.

I. PHYSICAL SMOKE ANALYSIS

We will continue with the smoke particle work, for which we have been developing a dilution system. This research will hopefully give us more quantitative information relating to the activation of smoke detection units, and to the transport of smoke aerosols throughout the facilities of concern.

J. FULL SCALE TESTS

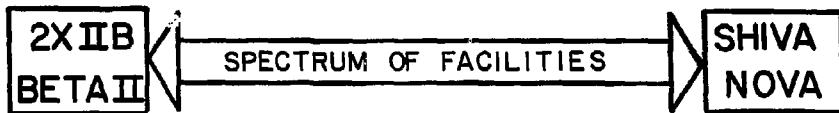
We intend to scale up our experiments to perform large scale cable burns to obtain more realistic data on the dynamics of burning cables. Although small scale tests are economical and very efficient they can rarely represent actual fire conditions. Ideally, deficiencies in small scale test results would dictate the design of large scale experiments and ultimately we would like to be able to correlate the results from both scales.

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- EXISTING ENCLOSURE
- EXISTING FPS
- LITTLE PASSIVE FIRE PROTECTION (FIRE RATED BARRIERS, SEPARATION, STOPS, CABLETRAYS).
- DEPENDENCE OF AUTO-MATIC SUPPRESSION SYSTEM.
- ENCLOSURE DESIGNED FOR EXPERIMENT.
- CONTEMPORARY FPS INCLUDED IN DESIGN PACKAGE.
- FIRE RATED BARRIERS AND OTHER PASSIVE PROTECTION.
- MULTI-FACET FPS STRATEGY, INDEPENDENT SYSTEM.

Fig. 1

GENERAL FLOW OF SYSTEMS APPROACH
TO FIRE RISK

CRITERIA:

USE BUILDING PASSIVE FIRE
PROTECTION AS A GUIDE.

DIVIDE BLDG. INTO
ZONES.

1

CRITERIA:

USE CAPITAL LOSS AND
PROGRAMMATIC DELAY AS
A GUIDE.

ASSESS SELECTED
ZONES FOR FIRE
IMPACT.

2

CRITERIA:

LLL AND DOE GUIDELINES
AND FIRE PROTECTION
ASSESSMENT ON A ZONE BY
ZONE BASIS.

ASSESS TOTAL EXPT,
FIRE IMPACT ACCP-
TABILITY.

3

CRITERIA:

IDENTIFY PROBLEM
AREAS AND COST
EFFECTIVE CHANGES
IN FP ACTIVITIES
TO BRING COSTS IN
LINE.

IDENTIFY COST EFFECT-
IVE SOLUTION TO IN-
CREASE FP ACTIVITIES
HARDWARE PERFORMANCE

4

Fig. 2

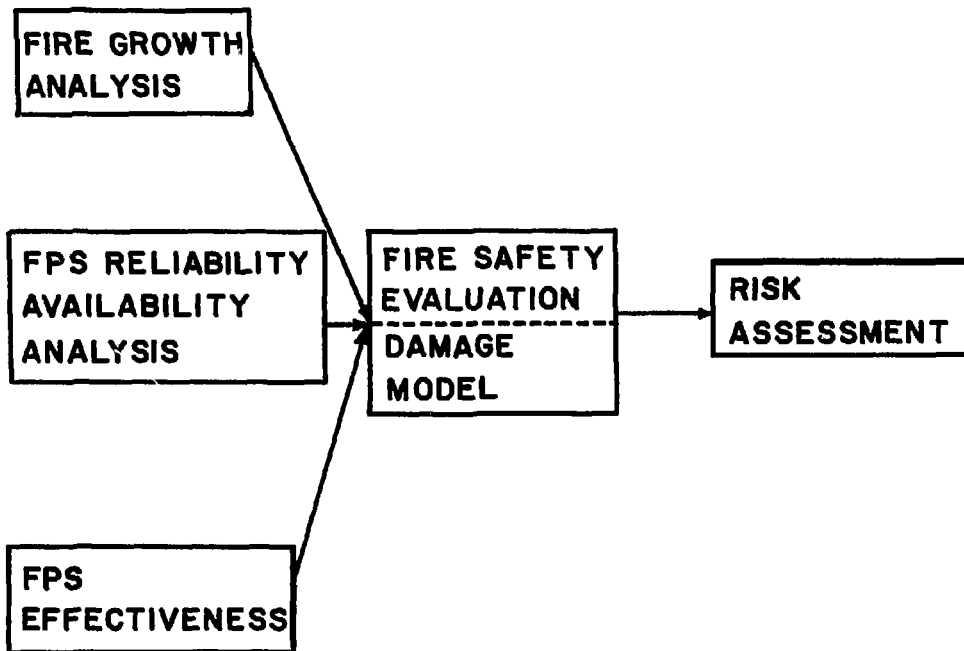
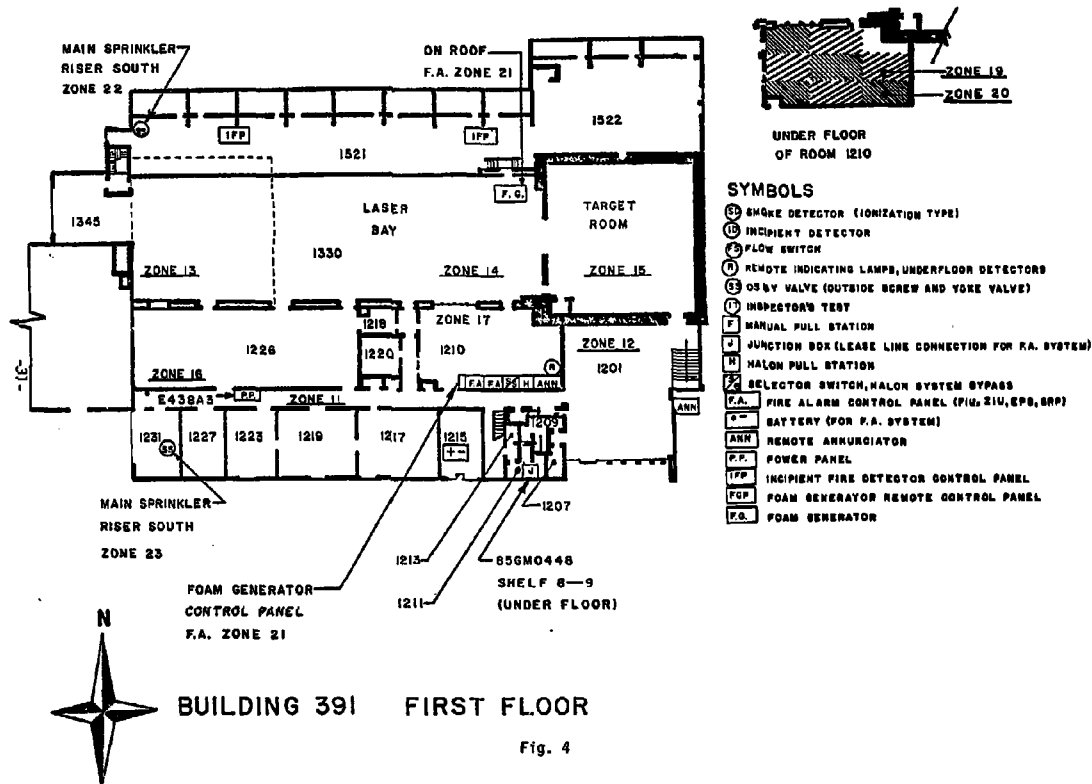
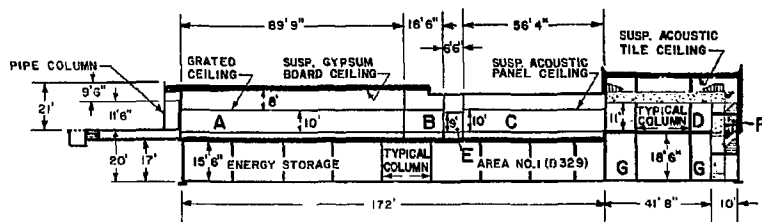


Fig. 3

FIRE ALARM DETECTOR SYSTEM ZONE LAYOUT



HIGH ENERGY LASER BUILDING 391 SECTION VIEW B



A—CLEAN LABORATORY 1226

E—CORRIDOR 1204

B—OFFICE 1220

F—STAIR NO. 2

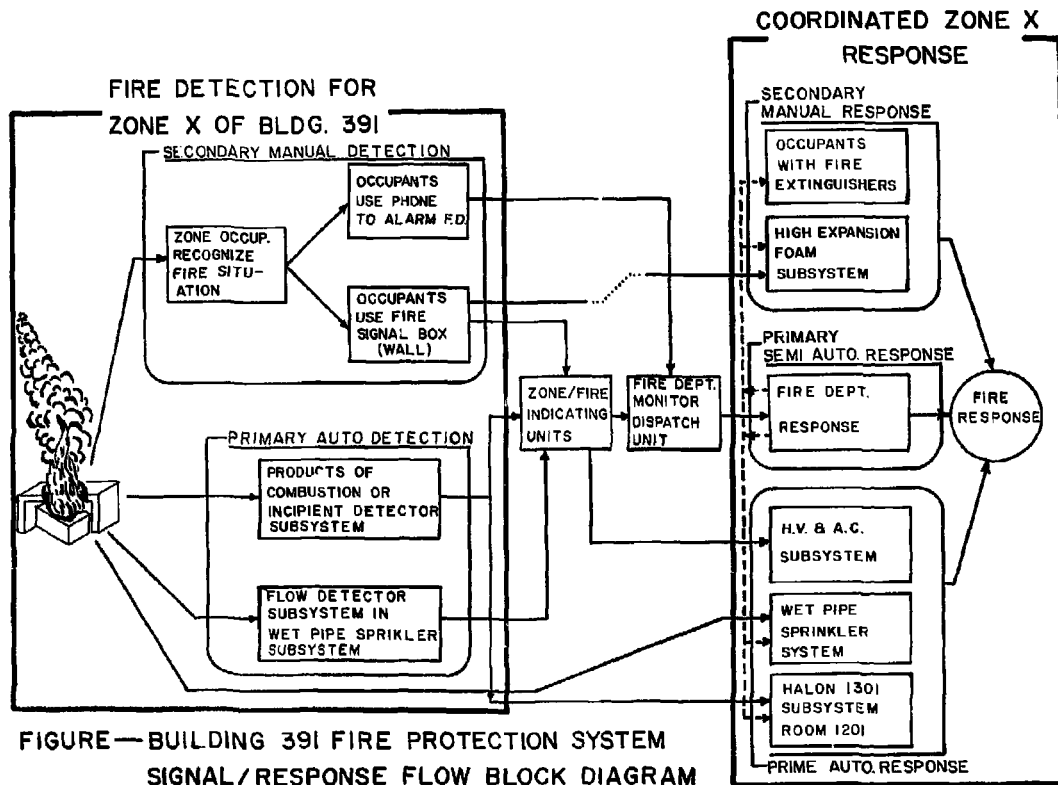
C—CONTROL AND DIAGNOSTICS 1210

G—ENERGY STORAGE AREA

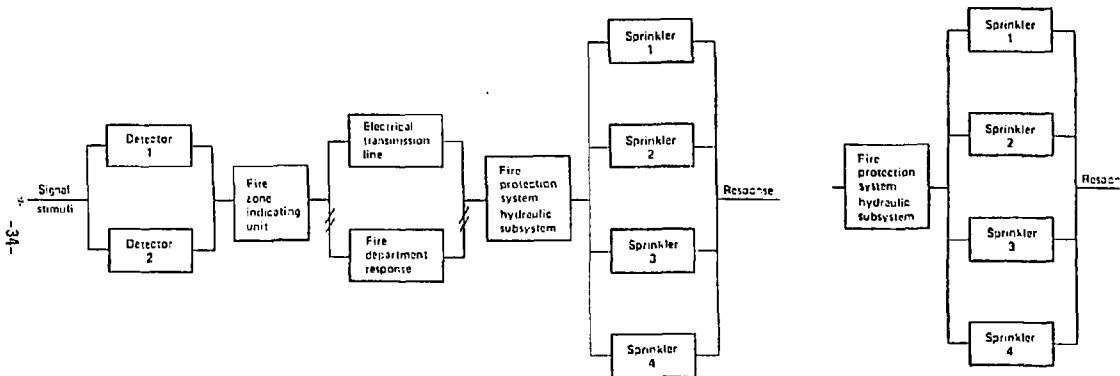
D—VISITOR AREA 1201

NO. 3 B 205

Fig. 5



**FIGURE—BUILDING 391 FIRE PROTECTION SYSTEM
SIGNAL/RESPONSE FLOW BLOCK DIAGRAM**



BLOCK DIAGRAM OF 2X2B's DRY-PIPE-PREACTION
SPRINKLER SYSTEM

BLOCK DIAGRAM OF SHIVA WET PIPE
SPRINKLER SYSTEM

Fig. 7

CABLE TYPES TESTED

(CROSS SECTIONS)

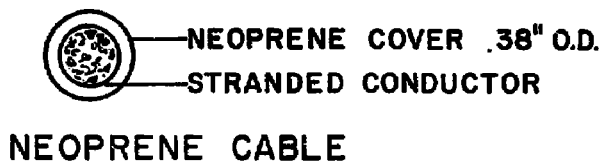
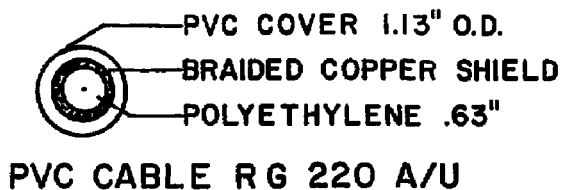
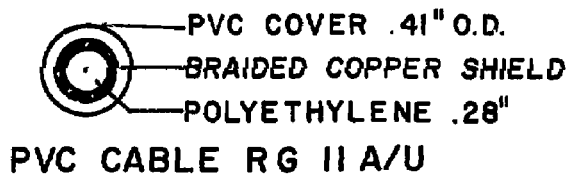


Fig. 8

SMALL SCALE FIRE TEST FACILITY

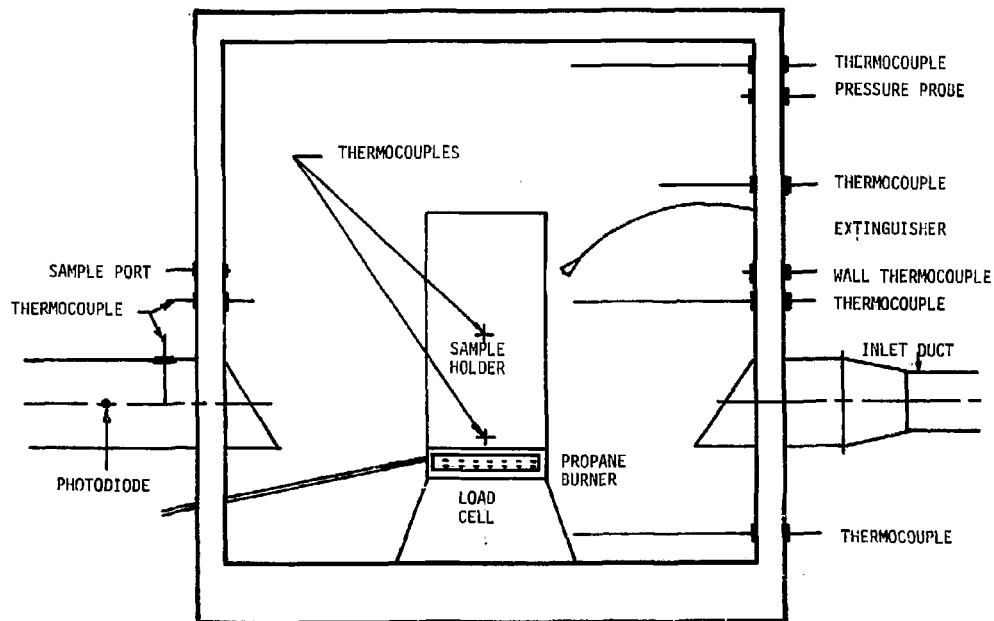
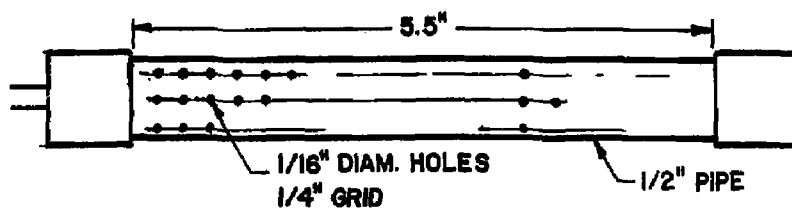
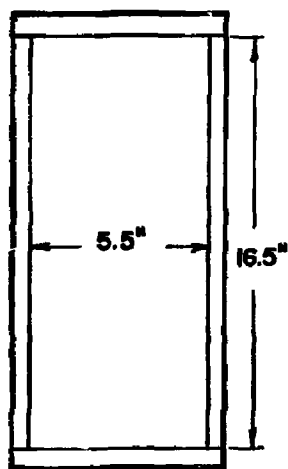


FIG. 9

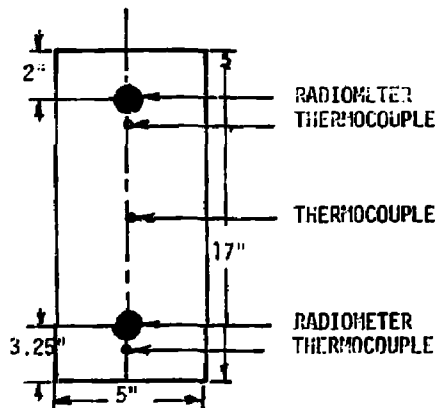


PIPE BURNER

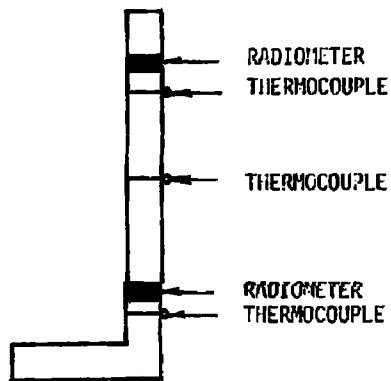


SAMPLE HOLDER FRAME EXPOSED
SURFACE

Fig. 10



CALIBRATION BOARD FRONT VIEW



CALIBRATION BOARD SIDE VIEW

FIG. 11

CALIBRATION CK.3

14-NOV-79

655 SEC DURATION

- CH 48 O-D. EXHAUST
- CH 45 PRESS. TOP OF BOX
- △ CH 46 PRESS MID OF BOX
- + CH 52 INLET FLOW
- x CH 66 RADIO METER IN BOX
- ◇ CH 67 RADIO. TOP OF CAL. BD.
- † CH 69 RADIO. BOTTOM OF CAL. BD.
- | CH 70 OXYGEN LEVEL IN BOX

OPTICAL DENSITY/METER

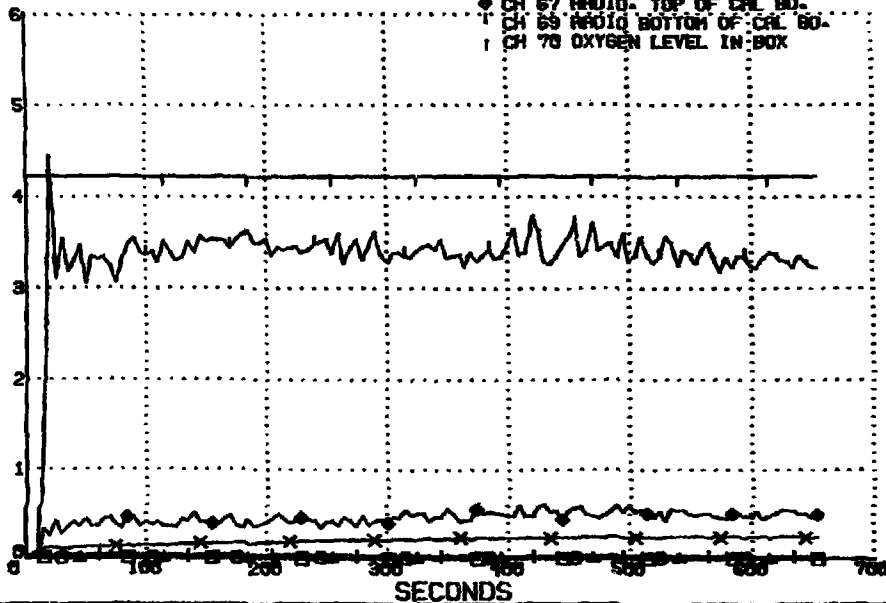


Fig. 12

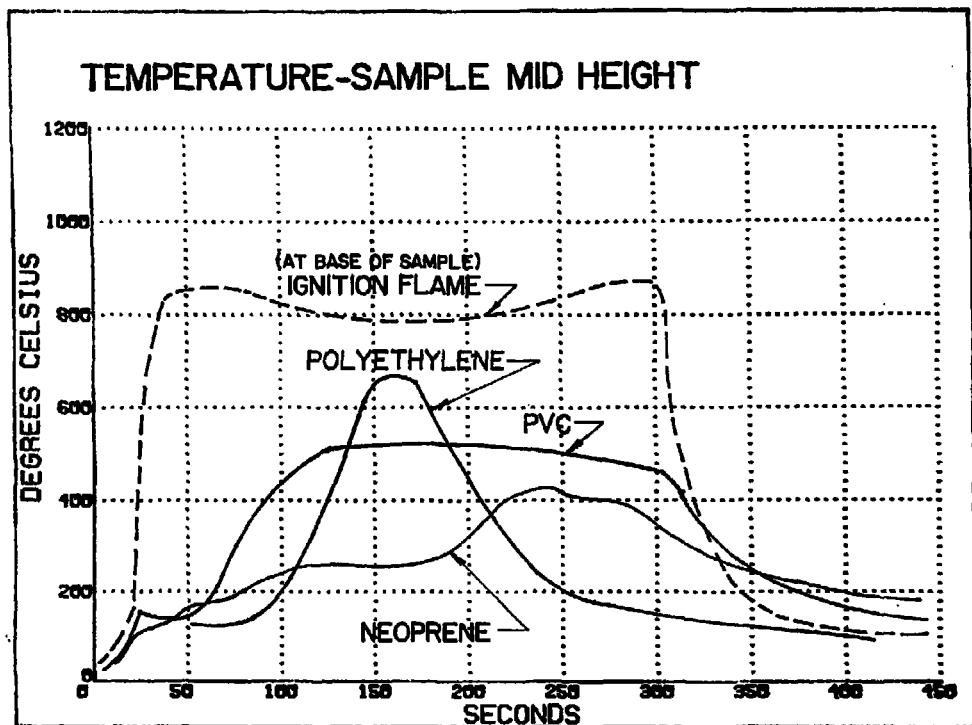


Fig. 13

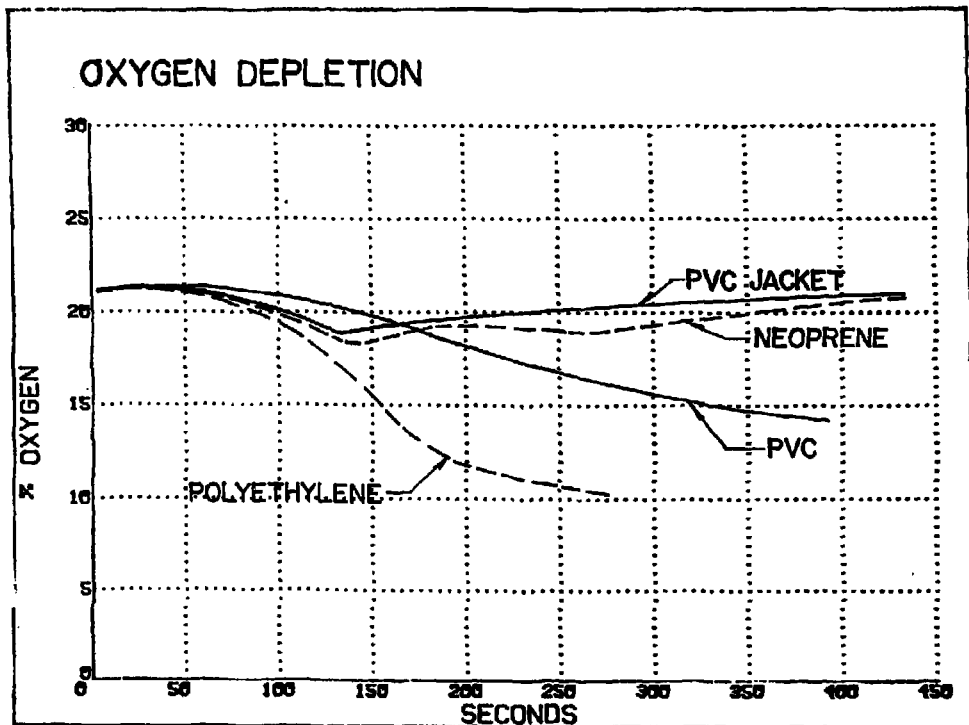


Fig. 14

PH OF COMBUSTION GASES

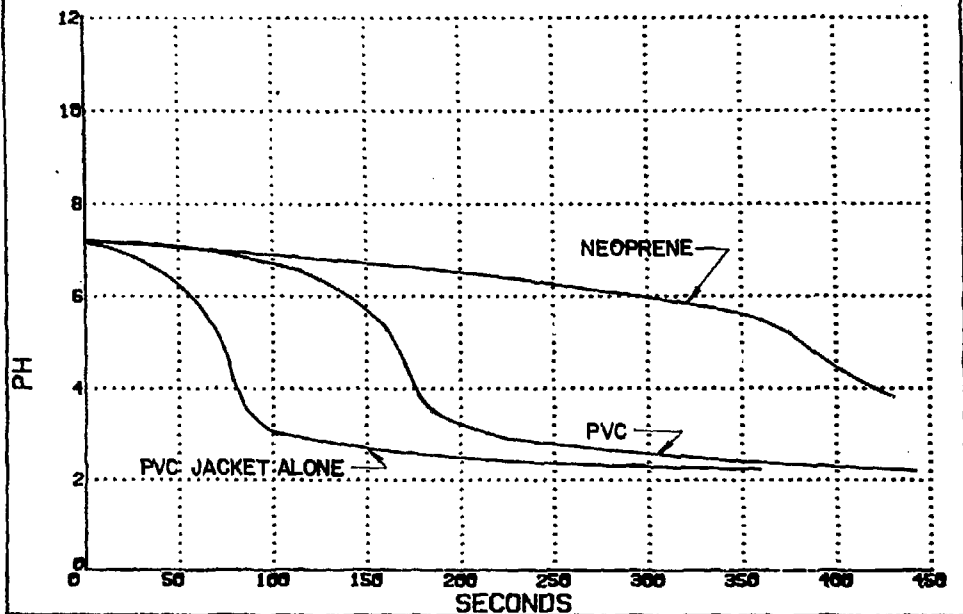


Fig. 15

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Table 6 Preliminary fault tree analysis results for SHIVA fire protection components.

Table 7 Comparison of analytical results to historical results.

Table 8 Results of small scale fire test facility tests.

Table 9 Listing of program objectives.

Table 1 Characteristics of Critical Spaces in SHIVA

Critical Space	Ceiling Height	Volume	Fire Hazard	Comments
LASER BAY	11.13 M (36.5')	8600M ³	Continuous volume high ceiling.	Extreme sensitivity of optics and electronics to fire products. High ceilings will slow automatic suppression. Low fuel load.
TARGET ROOM	16.61 M (54.5')	7134M ³	Continuous volume high ceiling	Lack of barriers allows fire growth. High ceilings will slow automatic suppression. But, fuel load is low.
CONTROL DIAGNOSTICS	3.05 M (10')	550M ³	High fuel load in relation to volume.	Sensitive electronics. Heart of experiment and also fire protection system. High potential loss.
ENERGY STORAGE #1	5.18 M (17')	1557M ³	High rack storage of oil filled capacitors	Communication through floor penetrations to Laser Bay. Most probable area for ignitions.

Table 2. LLNL SHIVA/NOVA EXPERIMENT

Potential Fuel Loads			
Critical Zones Max Delay and Economic Loss	Fuel Identification (in or adjacent zone)	Geometric Distribution Of Pyrolysing Fuel	Critical Components in Zone Susceptible to Damage
Laser Bay (L)	Cables 1) Insulation PVC 2) Dielectric 3) Neoprene Insulation acrylic and polyethylene films, paint, trash, solvents.	Widely distributed groupings.	Optical Equipment Mirrors Amplifiers and other Electronic, solid state equipment.
Target Bay (T)	Same as above	Widely distributed groupings.	Same as above
Control Room(C)	Computer printouts, trash, cabling, tape bin.	Widely distributed groupings.	Alignment firmware and software-computers Diagnostic electronics
Energy Storage (E)	PVC backings Capacitor oil in individual capacitors, cabling.	More or less uniform capacitors are stacked in steel shelves from ceiling to floor.	In zone-capacitors in adjacent zone above -optical equipment (see laser bay).

Table 3 Ventilation in SHIVA critical spaces.

<u>CRITICAL SPACE</u>	<u>VOLUME</u>	<u>MECHANICAL VENTILATION</u>	<u>CELLULOSE</u>	<u>PVC</u>
Laser Bay	8600M ³ (303,680 FT ³)	360 KCFM	1986 Kg.	1675
Target Room	7134 M ³ (251,954 FT ³)	195 KCFM	1648 Kg.	1388
Control/Diag.	550 M ³ (19,380 FT ³)	5.82 KCFM	127 Kg.	107
Energy Storage Area #1	1557 M ³ (54,973 FT ³)	10 KCFM	360 Kg.	303

Table 4 Shiva building 391 fire protection components.

SHIVA EXPERIMENT BUILDING AREA DESCRIPTION	BUILDING ZONE DESIGNATION	Applicable Fire Protection Subsystems					
		SPRKL SYS.	POC	DETECTORS MAN. ALARM	HV & AC CONTROL	HALON 1301	HIGH EX. FOAM
I. BASEMENT							
A. MECH./ELECT. EQUIP. ROOM	1	x	x	x			
B. ENERGY STORAGE AREA NO. 2	2	x	x	x			
C. ENERGY STORAGE AREA NO. 1	3,4	x	x	x			
E. TARGET BAY (BELOW RAISED FLR)	5	x	x	x			
F. ENERGY STORAGE AREA NO. 3	6	x	x	x			
II. FIRST FLOOR							
A. GEN. SUPPORT AREA 1	7	x	x	x			
B. GEN. SUPPORT AREA 2	8	x	x	x			
C. LASER BAY	9	x		x	x		
D. CLEAN LAB	10	x		x	x		
E. LABS	11	x	x	x			
COMP. CLEAN MECHANICAL ELECTRICAL FAN ROOM							
F. EXP. CONTROL RM. AND CLEAN DRESS PENETRATION	12A	x	x	x	x	x	
G. 1ST AND 2ND FLOOR GALLERY AND ENTRANCE	12B	x	x	x			
F. TARGET BAY (ABOVE RAISED FLOOR)	5	x	x	x	x		x

Table 5. SHIVA FIRE PROTECTION SYSTEM FTA RESULTS FOR SPECIFIC ZONES.

System Area	FPS Zone Unavailability (Per Demand)	Minimum No. of Subsystem Failures	
		For Entire FPS 6 A.M.-12 P.M.	"No Response" Outcome 12 P.M.-6 A.M.
LASER BAY (Spk1., IFD, Man. detect & response, ventilation) (Zones 13,14)	5.3×10^{-3}	3	2
TARGET BAY (Spk1., IFD, High ex-foam, man. detection & response, ventilation) (Zones 5,15)	5.9×10^{-3}	3	2
CAPACITOR BANKS (Sprinkler, POC, man. detect. & response) (Zones 3,4)	1.3×10^{-2}	3	2
CONTROL ROOM (Sprinkler, POC, man. detect. & response, Halon 1301) (Zones 17,18,19)	5.5×10^{-3}	3	2

Table 6 Preliminary fault tree analysis results for SHIVA fire protection components.

FPS SIGNAL-RESPONSE ANALYSIS

Major system subsystems	Availability per demand	Range of failures (F) of subsystem components for a "subsystem failure"
Halon 1301	-	$1 \leq F \leq 8$ for the most part these are supervised.
Incipient fire detection (IFD)	-	$1 \leq F \leq 2$ same as above.
ZIU/FIU	99%	$1 \leq F$ supervised by fire department.
Sprinkler(s) wet-pipe (without heads)	99.1%	$1 \leq F$ supervised by in-line pressure switches.

Table 7 Comparison of analytical results to historical results.

With NFPA and Factory Mutual Statistics

Data Source	Period	No. of Fires	% Satisfactory	FTA
NFPA	1924-1969	81,245	96.2	
AUSTRALIAN DATA	-	-	99.8	
UNITED KINGDOM	-	-	91.4	98%
FACTORY MUTUAL				
Wet Pipe	1970-1977	2,442	91.5	
Dry Pipe		757	86.0	82%
Pre-Action		7	85.7	

	PVC CABLE	P.E. INSULATION	PVC JACKET	NEOPRENE CABLE
TIME TO IGNITION	15-20 sec.	30-35 sec.	10-15 sec.	20 sec.
BURNING (SELF-SUSTAINING)	≥ 4 min.	≥ 2 min.	DID NOT AFTER <u>5</u> min.	DID NOT AFTER <u>5</u> min.
MAX. FLAME HEIGHT	10"	10"	10"	10"
COMBUSTION GASES	+ PRESSURE	+ PRESSURE	+ PRESSURE	NEUTRAL
O ₂	DOWN TO 14%	12%	19%	19%
PH	2 (FAST DROP)	7	2 (FAST DROP)	4 (SLOW DROP)
BURNER OUTPUT ≈ 87 BTU/MIN. (1531 J/S) PREMIXED PROPANE /AIR 5 MIN. ≈ 435 BTU. ≈ 4 W/CM ²				

Table 8 Results of small scale fire test facility tests.

Table 9 Program Objectives

- A. Major goal: Parallel development of fire safety with fusion energy technology.
- B. Define the Engineering performance of state of the art of fire protection as applied to fusion energy experiments.

FAULT TREE ANALYSIS

- C. Develop rational methods of assessing fault modes in fire protection systems.
- D. Develop techniques for defining fire hazards of fee.

FIRE GROWTH ANALYSIS

- E. Couple hazards analysis with fire protection systems analysis for LLNL facilities.

- F. Develop survey protocol for fee's at non-LLNL facilities and validate.

FIRE SAFETY EVALUATION

- G. Analyze survey results and evaluate fire safety of each installation.
- H. Conduct research to solve identified problems.

Appendix

THERMAL DEGRADATION OF WIRE AND CABLE INSULATIONS

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Livermore, California 94550

UCRL-84914, August 15, 1980

Summary

We investigated the thermal degradation of wire and cable insulations to determine the initial temperatures at which corrosive products are formed and the effect of different heating rates on their formation. Specifically we studied polyvinyl chloride (PVC) insulation for signal wire, PVC-polyethylene combination insulation and neoprene insulation for high-voltage cable, and Teflon insulation for cross-connect wire. Experimentation was preceded by a thorough literature search for information on oxidative and nonoxidative pyrolysis of these insulations and their basic polymers.

For a better understanding of the mode of decomposition of the insulations, we measured degradation products in air and in nitrogen using a thermogravimetric analyzer (TGA) and in air using a small fire test cell. We paid particular attention to corrosive gases since they can be detrimental to computer parts and high value optical equipment. Knowing the rate at which such gases are generated will help determine whether an existing insulation should be modified or replaced by a more heat-resistant material.

In addition to following the evolution of corrosive products during pyrolysis and combustion, we attempted to look at other degradation products that might be either highly flammable or toxic and therefore create an extra health hazard to fire fighters.

Results of this study show that (1) the initial decomposition temperatures of wire and cable insulations are to some extent governed by the additives in

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their formulations; (2) at high temperatures, Teflon is the most stable of all four materials tested, starting to decompose at 500°C; (3) air lowers the initial decomposition temperature of polyethylene but not that of Teflon, PVC, or neoprene; (4) heating rates affect the thermal degradation rates of all four insulations, but are most pronounced in PVC.

Introduction

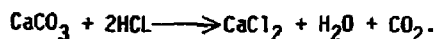
Before beginning our study on the thermal degradation of wire and cable insulations, we conducted a literature search for information on (1) the temperature range at which various insulations begin to generate corrosive products, (2) the rate at which they generate corrosive or flammable products, and (3) the effect of thermal irradiance and oxygen on the rate of product generation. We found a limited amount of literature on the thermodecomposition of wire and cable insulations emphasizing the generation of toxic products at predetermined temperatures but found nothing on initial decomposition of the basic polymers making up insulation materials.

Studies involving the decomposition of low-density polyethylene [1] (more commonly used in insulations than high-density polyethylene) show that this polymer starts decomposing at 350°C in vacuum and at 395° in nitrogen. Some researchers believe that the gaseous environment of nitrogen might cause a pressure dependence on the decomposition temperature and thus be responsible, at least in part, for the higher temperature observed. In the presence of oxygen, the decomposition temperature decreases drastically. Holmstrom and Sorvik [2] reported that polyethylene starts decomposing at 284°C when it is heated at atmospheric pressure in nitrogen containing 1.16% oxygen. They noticed a decrease in the intrinsic viscosity of polyethylene samples at 284°C and a shift toward lower molecular weights when the samples

are held at 355°C. They also observed a weight loss at temperatures as low as 315°C when the nitrogen was contaminated by 1.16% oxygen. The degradation products, formed through a chain scission resulting from inter- and intramolecular hydrogen abstractions, are saturated and unsaturated hydrocarbons, ethers, aldehydes, and ketones having low molecular weights.

Researchers who have studied the decomposition of PVC [3-8] report that its initial decomposition temperature varies between 120 and 170°C. The variation is a result of the purity of the polymer and the polymerization technique used to prepare it. There is a general agreement among the researchers that when PVC is heated to 220°C in a vacuum its only volatile degradation product is HCL. However, when it is heated to the same temperature in air, dehydrochlorination as well as oxidation reactions can occur and initiate chain scissions. Pyrolysis of PVC between 250 and 350°C results in the formation of HCL, benzene, toluene, and other hydrocarbons[5]. When PVC is preheated to 300°C for 30 min, the resulting degradation products are H₂, CO, saturated and -unsaturated hydrocarbons, styrene, substituted benzene, traces of ethylene chloride, and HCL [4].

McCormack [9], who studied the degradation of several neoprene compositions, showed that essentially all of the HCL in these compositions is liberated from the polymer chains at temperatures between 300 and 400°C. HCL is not detected in degrading neoprene that contains either CaCO₃ or CaCO₃ and Al₂O₃ + 3H₂O. The amount of CaCO₃ in the polymer is sufficiently large to react with most of the HCL potentially available from the neoprene compound. The initial major weight loss for neoprene compounds (at about 350°C) is believed to result from a loss of water rather than a loss of HCL, in accordance with the following reaction:



Studies on the pyrolysis of polytetrafluoroethylene (Teflon) [10-14] show

that this polymer is extremely stable below 350°C but decomposes rapidly at temperatures above 450°C. Its degradation products vary with the temperature of pyrolysis and the precise molecular weight of the polymer. Lee [10] and coworkers report that at 400°C Teflon loses only 0.04% of its weight and that its degradation products are HF and COF₂. At 450°C Teflon loses 3.56% of its weight and the main degradation product is a particulate product postulated to consist of the basic fluor-carbon matrix. In addition to the particulate product, gaseous tetrafluoroethylene (TFE) and hexafluoropropylene (HFP) are produced, both of which are respiratory toxins [10]. Between 500 and 550°C there is a shift in the pyrolysis products and octafluoroiso-butylene (OFIB), tetrafluoroethylene, hexafluoroethane (HFE), and hexafluoropropylene (HFP) [10]. Of these three products, OFIB is most toxic, causing respiratory damage and kidney damage [11]. Above 500°C, the entire degradation product is thought to be carbonyl fluoride. This compound may react with the glass parts of experimental equipment to produce silicon tetrafluoride. The toxicity of both of these compounds appears to be limited to the lungs [12].

Experimental Approach

The experimental approach consisted of:

1. Thermogravimetric analysis of the various insulations in nitrogen and in air at heating rates of 2.5, 5, 10, 20, and 40°C/min from ambient to 900°C.
2. Monitoring of corrosive products during thermogravimetric measurements to determine the initial temperature of their generation and the effect of air and heating rates on their evolution.
3. Monitoring of corrosive products at the entry of the ductwork of the small test cell.

4. Gas chromatographic/mass spectrometric analysis of the noncorrosive thermal degradation products.

Experimental Procedure

PVC, PVC-polyethylene, neoprene, and Teflon samples weighing 8-10 mg were, heated at a rate of 2.5-40°C/min in dry nitrogen and dry air from ambient temperature to 900°C in a thermogravimetric analyzer (TGA). This particular TGA model has a temperature capability up to 1000°C. A multi-channel recorder recorded sample weight as a function of temperature and the rate of change in sample weight, measured by our derivative computer. The thermal degradation gases produced by the samples in the TGA were directed to a 50-ml test tube filled with 20 ml of distilled water, buffered to pH 6.8-7.0. The aqueous solution was gently stirred with a magnetic stirrer to achieve uniform mixing. The change in pH (predominantly caused by the formation of HCL) was measured with a pencil-size pH-reference electrode as a function of temperature and recorded by the multichannel recorder, together with the weight loss of the sample. This simple approach gave us a visual correlation between weight loss, the generation of corrosive gases, and the initial temperature at which these gases are formed.

Next, we measured the HCL and other combustion products generated from heated samples in the small test facility. The facility as shown in figure 1 has an overall volume of 0.42 m³(15 ft³) and is equipped with 152 mm(6") diameter ventilation ducts that extend approximately 1.8 m(6') from both sides. Air can either be forced or drawn through the box. The principle parameters which can be monitored during an experiment are: airflow, optical density, enclosure pressure, fuel mass loss, temperatures and flame radiation. Combustion products are drawn from a point near the exhaust duct. Figure 2 shows the location of the various sensing devices in and on the cell along with the test specimen and gas burner.



Fig. 1

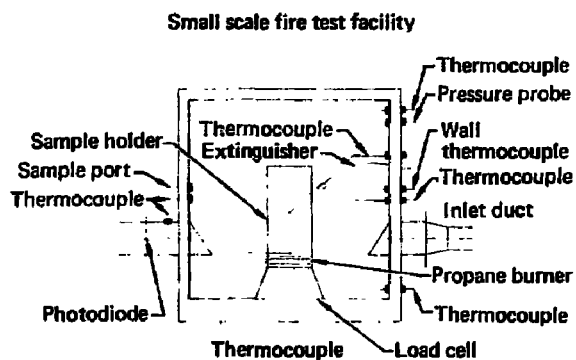


Fig. 2

Each test sample consisted of eight neoprene or PVC cable insulations held in place in a specially designed holder. Each cable was 45 mm(18") long and had an O.D. of 10 mm (3/8"). The gas burner was 12.7mm (1/2") diameter pipe with 1.6mm(1/16") holes drilled on a 6.4mm(1/4") grid. Its output was a premixed propane/air flame with an energy output of approximately 1530J/s (908BTU/min) which gives a total 5 minute run of 459 BTU.

During an experiment, combustion products were sampled with a vacuum pump and bubbled into 40 ml of distilled water buffered to pH 6.8-7.0.

A pH-reference electrode was connected to an Orion digital meter and a PDP-11 computer, which also recorded temperatures, weight loss, oxygen depletion and temperature rise as a function of time.

Two methods were used to determine the noncorrosive thermal degradation products of the plastics. One involved extracting the aqueous sample with cyclohexane, condensing the extract, and analyzing the solution in a gas chromatograph/mass spectrometer (GC/MS). The other involved heating the sample which weighed approximately (0.5 mg) in a pyrolyzer and allowing the products to enter a gas chromatographic (gc) column shortly after pyrolysis. Only the PVC and polyethylene samples were thermally degraded in the pyrolyzer.

The PVC sample was first placed in the TGA and heated in N_2 at $20^{\circ}C/min$ to $355^{\circ}C$ to drive off most of the HCL, and then placed in the pyrolyzer and heated in helium at $360^{\circ}C$ to determine what other products form from the dehalogenated hydrocarbon and the remaining additives incorporated into the plastic during the manufacturing process. Since polyethylene starts decomposing at $230^{\circ}C$ in air and is widely used in combination with PVC for insulating high-voltage cables, we pyrolyzed a polyethylene sample at $230^{\circ}C$ to determine the kinds of degradation products that form at the onset of pyrolysis or combustion.

The products from all samples were separated on a 6-ft x 1/8-in. stainless-steel column packed with 4% SE-30 on 100/20 supelcoport and on a 6-ft x 1/8-in. stainless-steel column packed with 4% Carbowax 20 M on 80/100 Chromosorb WAW. Two microliters of the solution were injected on the columns for each analysis. To separate the more volatile fractions, initial column temperature was set at 40°C and programmed at 2°C/min to 150°C; helium flow rate was maintained at 20 ml/min; and the injection port, flame ionization detector oven, mass spec transfer line, and jet separator oven were set at 250°C. To separate the less volatile fractions, initial column temperature was set at 100°C and programmed at 5°C/min to 240°C and helium flow rate was maintained at 40 ml/min, the other parameters remained the same as in the separation of the more volatile fraction.

Results

Figure 3 shows the dynamic thermogravimetric weight as a function of temperature for the various polymers heated in nitrogen at 10°C/min. Cellulose is included for comparison. The curves disclose the threshold temperatures for active pyrolysis as well as the temperature ranges at which the majority of the degradations occur. Teflon was the most stable insulation, followed by polyethylene, cellulose, PVC, and neoprene. A more detailed examination of the individual weight loss curves reveals certain differences among the insulations.

The neoprene-based insulation shows three distinct regions of decomposition. The first region, an initial rapid weight loss between 180 and 280°C, is probably caused by a loss of water from hydrated alumina, one of the additives frequently included in the neoprene composition. The second region of decomposition takes place between 280 and 380°C and is attributed

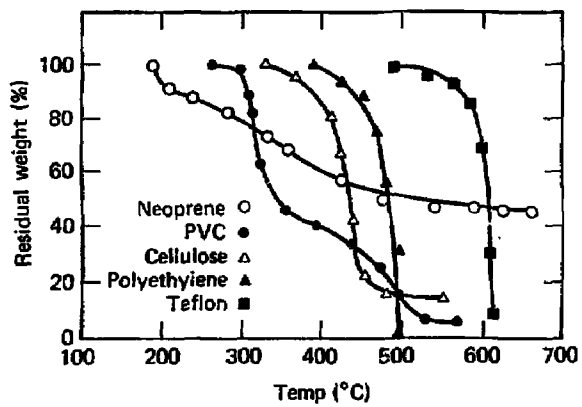


Fig. 3

to the loss of HCL from the polymer chain. The third region, a very gradual weight loss, is probably caused by the decomposition of carbonaceous residue in the polymer chain.

The polyvinylchloride insulation also shows three regions of decomposition. The first region, the initial rapid weight loss between 260 and 350°, is primarily the result of a loss of HCL and the degradation of a plasticizer usually included in the PVC preparation. The dehydrochlorination reaction leads to the formation of long, conjugated polyenyl structures. The second region, between 350 and 510°C, involves the decomposition of the residual cross-linked polymer chains. Finally, the third region, a very slow degradation of the polymer's charlike residue, commences at 520°C.

The initial decomposition of polyethylene between 390 and 450°C suggests zero-order kinetics and is probably caused by segments breaking off the ends of the highly branched polymers as well as decomposition of additives incorporated in the formulation. The next region, between 450 and 500°C, resembles first-order kinetics and is probably caused by random breaking of the molecular chain.

The dynamic thermogravimetric curve for Teflon shows the exceptional thermal stability of the polymer. In the nitrogen environment Teflon loses very little weight until 500°C, and the maximum degradation rate occurs from approximately 580 to 650°C. The degradation of this insulation material appears to follow first order kinetics during the main portion of decomposition. It is believed that the basic polymer begins to decompose or "unzip" at the free radical ends of the chain, yielding mostly monomers. Once started, the polymer continues to unzip down the chain until the whole chain has decomposed.

Figure 4 compares the rate of change in residual weight with the rate of decomposition for PVC insulation heated in nitrogen at $10^{\circ}\text{C}/\text{min}$. The rate of change in weight is depicted as the percentage of weight loss per minute and as a function of the heating rate. Portraying the degradation of insulation materials in this way gave us a clear view of how the polymer might be affected by air or different heating rates. The graph shows that the highest rate of degradation is between 290 and 340°C , the range in which dehydrochlorination occurs, and between 440 and 500°C , the range in which decomposition of residual polyenyl structure occurs.

Neoprene

Figure 5 shows the effect of the heating rate on the degradation of neoprene in nitrogen. An increased heating rate has no effect on the initial degradation temperature, which remains at 170°C ; however, it has a pronounced effect on the rate of dehydrochlorination in the region between 280 and 350°C and on the rate of oxidation of carbonaceous residue in the region between 450 and 550°C . When the sample is heated at a rate of $40^{\circ}\text{C}/\text{min}$, the rate of degradation during dehydrochlorination and oxidation of the residual polymer chain increases drastically, peaking at 430°C to $12\%/ \text{min}$. However when the sample is heated at a rate of $20^{\circ}\text{C}/\text{min}$, the rate at 430°C is only $1\%/ \text{min}$.

The effect of air on the degradation of neoprene (Fig. 6) is most pronounced when the sample is at the rates of 20 and $40^{\circ}\text{C}/\text{min}$. Again, the rate of degradation is influenced most during dehydrochlorination and oxidation of the carbonaceous residue in the region between 500 and 600°C . The initial degradation temperature remains unchanged.

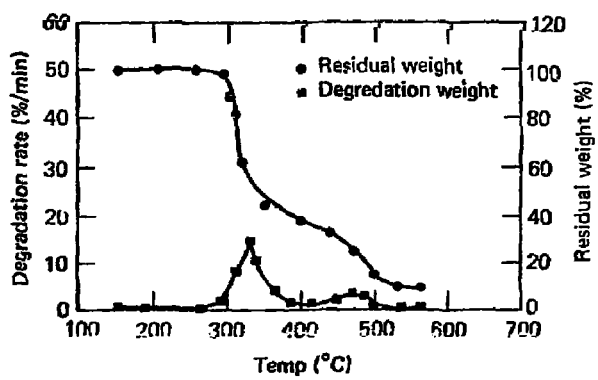


Fig. 4

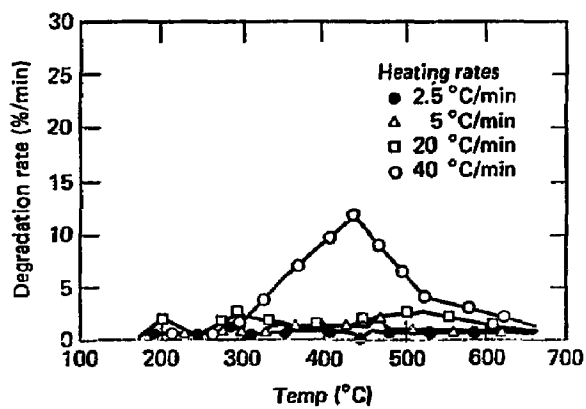


Fig. 5

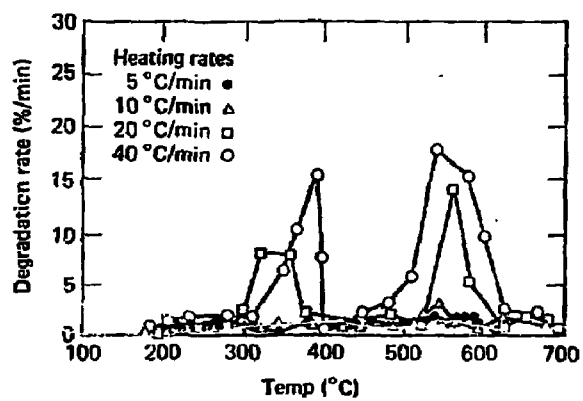


Fig. 6

Figure 7 shows that there was no change in the pH of the solution during decomposition of the neoprene sample heated in air at 10°C/min in the TGA. As mentioned previously, the HCL that evolves reacts with the CaCO_3 incorporated in the sample and therefore remains undetected by the pH meter. Similarly, no HCL was detected when the neoprene insulation was burned in the small test facility.

In addition to HCL, we measured other combustion products from burning neoprene--those from residual neoprene polymer and those from additives used in the formulation of neoprene. The airborne products were bubbled into a water trap and extracted with cyclohexane before GC/MS analysis. Table 1 lists some of these products and their probable health, flammability, and reactivity hazards. The hazards, assigned according to the recommendations of the National Fire Protection Association (NFPA) [15], are those that might be encountered by firemen fighting fires involving plastic insulation materials.

The system used by the NFPA identifies the hazards of a chemical in terms of three categories; namely "Health, Flammability, and Reactivity" and indicates the order of severity in each of these categories by five divisions ranging from "four (4)" indicating a severe hazard to "zero (0)" indicating no special hazard.

The chemicals listed in Table 1 are, for the most part, decomposition products of residual neoprene polymer and additives used in neoprene formulation so most of the products are nonreactive and must be moderately heated in order to ignite. Phenol and *p*-cresol are extremely hazardous if they come in contact with the skin. Therefore, firefighters should wear full protective clothing--plus selfcontained breathing apparatus; rubber gloves; boots; and bands around legs, arms, and waist.

Polyvinylchloride

Figure 8 shows the effect of heating rates on the degradation of PVC in nitrogen. The increased heating rates have their greatest affect on decomposition rates in the dehydrochlorination range which occurs between 260 and 350°C. The increased heating rates also affect the rate of

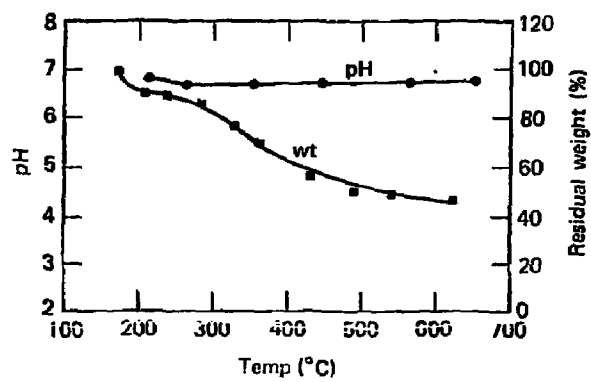


Fig. 7

Table 1. Thermal degradation products of neoprene generated in a small test facility.

Degradation product	NFPA Hazard Identification		
	Health	Flammability	Reactivity
phenol	3 ^a	2 ^e	0 ^g
<u>o</u> -cresol	3	2	0
benzylcyanide	2 ^b	1 ^f	0
<u>p</u> -methylbenzyl alcohol	1 ^c	1	0
<u>n</u> -pentacontanoic acid	2	1	0
hexacosanol-1		no data	
1,2-dicyanobenzene		no data	
phthalonitrile		no data	
isophthalonitrile		no data	
7-methylquinoline	2	1	0
triacontane		no data	
11- <u>n</u> -decyl docosane		no data	
11- <u>n</u> -decyl tetracosane		no data	
<u>n</u> -octacosane		no data	
<u>n</u> -hexatriacontane		no data	
dioctylphthalate	0 ^d	1	0
1-methyl-cis-4-ethylcyclohexane		no data	

^aChemical is extremely dangerous, but protective clothing; self-contained breathing apparatus; rubber gloves; boots; and bands around arms, legs, and waist will provide protection.

^bChemical is hazardous when inhaled, but self-contained breathing apparatus will protect against inhalation.

^cChemical is only slightly hazardous to firemen.

^dIn a fire condition, chemical would pose the same health hazard as an ordinary combustible material.

^eChemical must be moderately heated to ignite. Water may extinguish the fire because the chemical can be cooled below its flash point.

^fChemical must be preheated to ignite. Water may cause frothing if it gets below the surface of the liquid and turns to steam. A water fog gently applied to the surface will cause frothing that will extinguish the fire.

^gChemical is normally stable and therefore does not present any reactivity hazard to firemen.

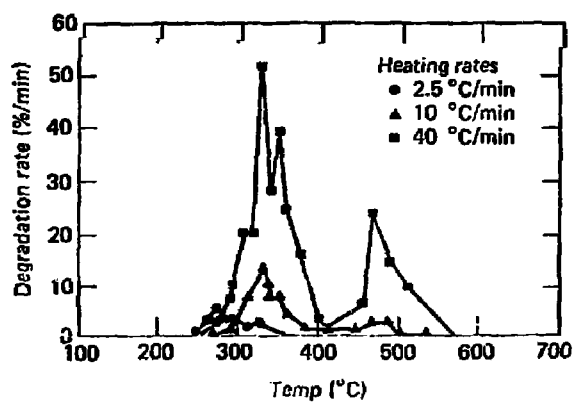


Fig. 8

decomposition of the highly cross-linked carbonaceous chain which takes place in the temperature range between 350 and 510°C. The higher heating rates do not change the initial decomposition temperatures which remains at 250°C.

The effect of air on the decomposition rate of PVC (Fig. 9) is most pronounced in the active pyrolysis region or the dehydrochlorination region. This is particularly evident at a heating rate of 40°C/min, which leads to a peak decomposition rate of 50%/min. At a heating rate of 20°C/min, the peak decomposition rate is only 10%/min.

Figure 10 shows the evolution of HCL from a PVC sample heated in nitrogen at 10°C/min. The HCL first evolves at a low rate at 195°C and then increases in rate between 290 and 310°C, and finally reaches a constant level at 370°C.

To determine the other degradation products of PVC, i.e., those formed after most of the HCL has left, we heated a sample of PVC insulation in the IGA to 355°C and then pyrolyzed its residue in helium at 340°C in a pyrolyzer directly connected to the inlet system of our gas chromatograph. We used helium in the pyrolyzer since it was already being used to separate the mixture on the gc column.

The products we identified (Table 2) are formed during the decomposition of highly cross-linked polyenyl residue. Most of the chemicals are hazardous when inhaled, but their inhalation can be avoided by the use of a self-contained breathing apparatus. Some, such as isoprene and cyclopentadiene, are very flammable and capable of violent chemical change at elevated temperature and pressure. Others, for example, benzene, toluene, chlorobenzene, *o*, *m*, *p*-xylene and styrene, are liquids that can be ignited under almost all normal temperature conditions. The rest of the products are either chemicals that must be moderately heated before they can ignite or chemicals that will not burn.

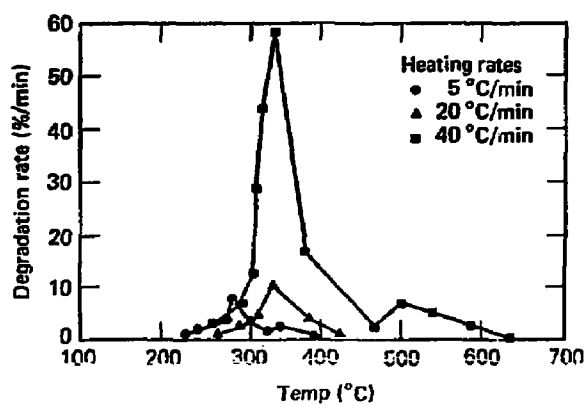


Fig. 9

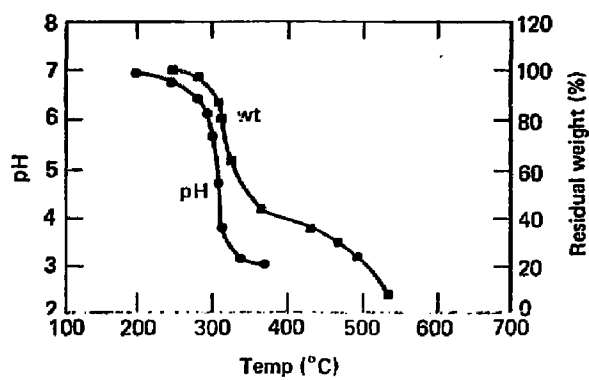


Fig. 10

Table 2. Thermal degradation products of PVC pyrolyzed in helium at 360°C

Degradation product	NFPA Hazard Identification		
	Health	Flammability	Reactivity
1,3-butadiene	2 ^a	4 ^c	2 ^g
isoprene	2	4	2
cyclopentadiene		no data	
benzene	2	3 ^d	0 ^h
toluene	2	3	0
chlorobenzene	2	3	0
<u>o,m,p</u> -xylene	2	3	0
styrene	2	3	2
o-methylstyrene	2	2 ^e	0
1-methylnaphthalene	2	2	0
biphenyl	2	1 ^f	0
fluorene		no data	
phenanthrene	-	1	0
anthracene	0 ^b	1	-

^aChemical is hazardous when inhaled, but self-contained breathing apparatus will protect against inhalation.

^bIn a fire condition, chemical would pose the same health hazard as an ordinary combustible material.

^cChemical is a very flammable gas or liquid.

^dChemical can be ignited under almost all normal temperature conditions. Water may not extinguish the fire because of the chemical's low flash point.

^eChemical must be moderately heated to ignite. Water may extinguish the fire because the chemical can be cooled below its flash point.

^fChemical must be preheated to ignite. Water may cause frothing if it gets below the surface of the liquid and turns to steam. A water fog gently applied to the surface will cause frothing that will extinguish the fire.

^gChemical undergoes a violent chemical change at elevated temperatures and pressures.

^hChemical is normally stable and therefore does not present any reactivity hazard to firemen.

Figure 11 shows the rise in temperature in the proximity of a PVC sample burned in the small fire test facility and the pH of the gas stream. The sample was the PVC portion of the composite PVC-polyethylene cable insulation. The initial change in pH occurs 15 seconds after ignition, when the temperatures near the bottom and center of the sample are 340°C. Hydrochloric acid stops evolving at 100 seconds after ignition, when the temperature near the bottom of the sample is 400°C and the temperature near the center of the sample is 520°C. We feel that the discrepancy between the measured initial temperatures for the evolution of HCL in the small test facility and the TGA is partly because in the small test facility the HCL is measured under flaming combustion and in the TGA, the HCL is measured under smoldering or pyrolyzing conditions. In the small test facility the thermocouples measure both sample temperature and flame temperature as the flames move across the surface of the sample. The thermocouple in the TGA furnace is situated closer to the sample and therefore measures the increase in sample temperature fairly accurately, as the temperature of the furnace is increased in a controlled linear fashion. In the test facility the temperature rise on the surface of the sample is so rapid that the temperature during pyrolysis, preceeding flaming combustion, cannot be resolved; and thus, early dehydrochlorination, which would occur at a lower temperature, for example, 195±5°C, remains undetected. Nevertheless, the two apparatus can be used successfully to estimate the initial temperatures at which HCL is produced during a cable shortout and to determine the time at which HCL is produced after ignition of the sample.

Table 3 lists some of the combustion products from flaming PVC insulation. The products were collected in water and extracted with cyclohexane from the aqueous solution before GC/MS analysis. An overall

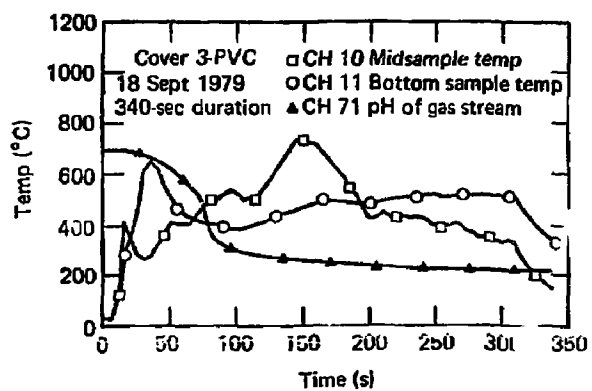


Fig. 11

Table 3. Thermal degradation products of PVC insulation generated in a small test facility

Degradation product	NFPA Hazard Identification		
	Health	Flammability	Reactivity
methylcyclohexane	2 ^a	3 ^d	0 ^g
cyclohexane	1 ^b	3	0
<i>o</i> -methylbenzyl alcohol	1	1	0
6-tert-butyl- <i>m</i> -cresol	2	2 ^e	0
<i>o</i> -sec-butylphenol	1	1 ^f	0
<i>p</i> -isopropylbenzoic acid		no data	
1-naphthylhendecane		no data	
biphenylene	2	1	0
ethylphthalate	0 ^c	1	0
diethylphthalate	0	1	0
fluorene		no data	
anthracene	0	1	-
phenanthrene	-	1	0
2-azidobiphenyl	-	1	0
2,2-bis (p-hydroxyphenyl) propane		no data	

^aChemical is hazardous when inhaled, but self-contained breathing apparatus will protect against inhalation.

^bChemical is only slightly hazardous to firemen.

^cIn a fire condition, chemical would pose the same health hazard as an ordinary combustible material.

^dChemical can be ignited under almost all normal temperature conditions. Water may not extinguish the fire because of the chemical's low flash point.

^eChemical must be moderately heated to ignite. Water may extinguish the fire because the chemical can be cooled below its flash point.

^fChemical must be preheated to ignite. Water may cause frothing if it gets below the surface of the liquid and turns to steam. A water fog gently applied to the surface will cause frothing that will extinguish the fire.

^gChemical is normally stable and therefore does not present any reactivity hazard to firemen.

appraisal of the products indicates that most of these compounds are probably formed during degradation of the residual highly cross-linked PVC polymer, after most of the HCL has left the polymer. It is also conceivable that some of them, e.g., ethylphthalate and diethylphthalate, are volatilized plasticizers used in the formulation of PVC. A few of the noncorrosive chemicals formed during combustion are hazardous when inhaled, so firemen must wear self-contained breathing apparatus. Methylcyclohexane and cyclohexane are two examples of chemicals which can be ignited under almost all of the normal temperature conditions.

Polyethylene

Figures 12 and 13 show the effect of heating rates and air on the pyrolysis rate of polyethylene. As with the other insulations, the heating rate does not affect the initial decomposition temperature (380°C in nitrogen and 230°C in air). Raising the heating rate from $2.5^{\circ}\text{C}/\text{min}$ to $10^{\circ}\text{C}/\text{min}$ increases the rate of random breaking in the molecular chain between 435 and 480°C . Polyethylene starts decomposing considerably earlier in air than in nitrogen. All heating rates show very low decomposition rates at 230°C ; however, when they are raised to 1, 20, and $40^{\circ}\text{C}/\text{min}$ at 380, 375, and 360°C , respectively, the decomposition rates increase rapidly. Figure 13 also shows that the maximum weight loss rates largely depend on the heating rate of the sample.

Table 4 lists a number of the decomposition products of polyethylene that form in helium at 380°C . Most of the chemicals are nonreactive but have a very low flashpoint and will ignite under almost all normal temperature conditions. A number of these compounds are dangerous when inhaled; hence a self-contained breathing apparatus is required for protection against them.

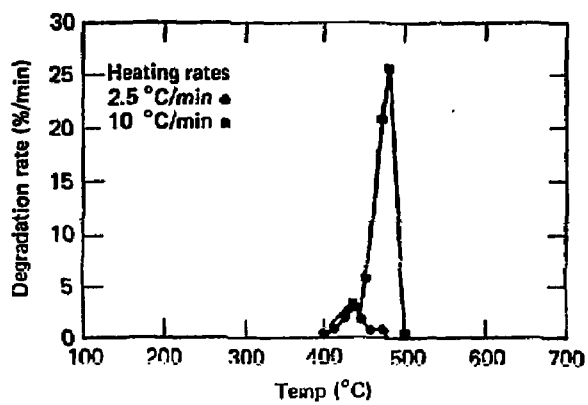


Fig. 12

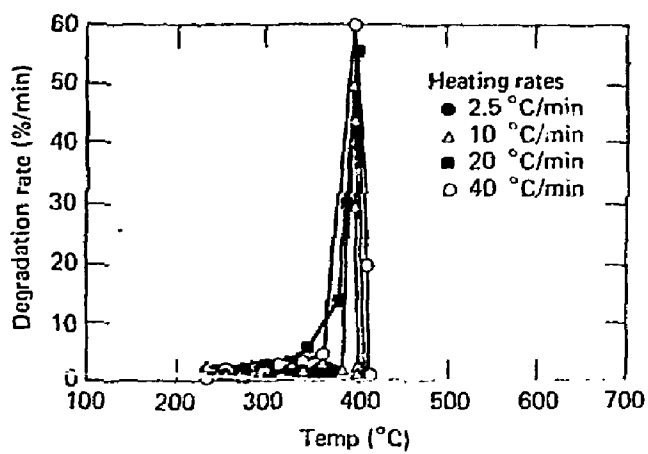


Fig. 13

Table 4. Thermal degradation products of polyethylene pyrolyzed in helium
380°C.

Degradation product	NFPA Hazard Identification		
	Health	Flammability	Reactivity
1-butyne	-	4 ^d	-
cis and trans-2-butene	1	4	0
2-methyl-2-butene	2a	3 ^e	0
1,1-dimethyl-cyclopropane		no data	
1,4-pentadiene	0	4	2 ^h
1-pentene	0	4	-
isoprene	2	4	2
1-cis-3-pentadiene	0	4	2
propenylacetylene		no data	
cyclopentane	1 ^b	3	0 ⁱ
1-hexyne		no data	
2-methyl-1-pentene	1	3	0
2,4-hexadiene	0 ^c	3	0
2-methylpent-3-en-1-yne		no data	
1,3,5-hexatriene		no data	
benzene	2	3	0
1,4-cyclohexadiene		no data	
cyclohexene	1	3	0
1,trans-2-dimethylcyclopentane		no data	
1-heptene	0	3	0
2-methyl-1,5-hexadiene		no data	
vinylcyclopentane		no data	
1,2-dimethylcyclopentadiene		no data	
toluene	2	3	0
bicyclo(5,2,1) octane		no data	
ethylbenzene	2	3	0
o and p-xylene	2	3	0
styrene	2	3	2
1-nonene	0	3	0
o-methylstyrene	2	2 ^f	0
4'-methylphenylacetylene		no data	
1,9-nonanediol		no data	
1-undecanol	1	19	0

^dChemical is hazardous when inhaled, but self-contained breathing apparatus will protect against inhalation.

^bChemical is only slightly hazardous.

^cIn a fire condition, chemical would pose the same health hazard as an ordinary combustible material.

^dChemical is a very flammable gas or liquid.

^eChemical can be ignited under almost all normal temperature conditions. Water may not extinguish the fire because of the chemical's low flash point.

^fChemical must be moderately heated to ignite. Water may extinguish the fire because the chemical can be cooled below its flash point.

Table 4 Cont.

⁹Chemical must be preheated to ignite. Water may cause frothing if it gets below the surface of the liquid and turns to steam. A water fog gently applied to the surface will cause frothing that will extinguish the fire.

^hChemical undergoes a violent chemical change at elevated temperatures and pressures.

ⁱChemical is normally stable and therefore does not present any reactivity hazard to firemen.

Teflon

Figures 14 and 15 show the decomposition of teflon in nitrogen and in air. Unfortunately, at this point in our study, we experimented with only two heating rates in nitrogen and three heating rates in air. In nitrogen, a change from 2.5 to 10°C/min causes the temperature at which the maximum rate of degradation occurs to shift from 565, to 600°C. At a heating rate of 2.5°C/min air does not affect the temperature at which the maximum rate of degradation occurs, but it does change the rate of degradation from 7 to 10%/min. A heating rate of 10°C/min lowers the temperature at which the maximum rate of weight loss occurs from 620°C to 600°C in air. The maximum rate of weight loss in air at a heating of 10°C/min is 29%/min, as opposed to 20%/min in nitrogen at the same heating rate. A heating rate of 20°C/min in air shifts the temperature at which maximum weight loss occurs to 630°C. The maximum rate of degradation at this temperature is 47%/min.

The decomposition products of Teflon were not analyzed.

Conclusions

The primary findings of this study indicate the following:

1. The initial decomposition temperatures of wire and cable insulation materials are to some extent governed by the additives present in the formulations and therefore are not exactly the same as those reported in literature for the basic polymers.
2. The techniques used to determine the initial temperatures at which corrosive products are formed can be successfully applied to pyrolysis studies. However, the initial temperatures at which corrosive chemicals are given off during flaming combustion cannot be determined accurately

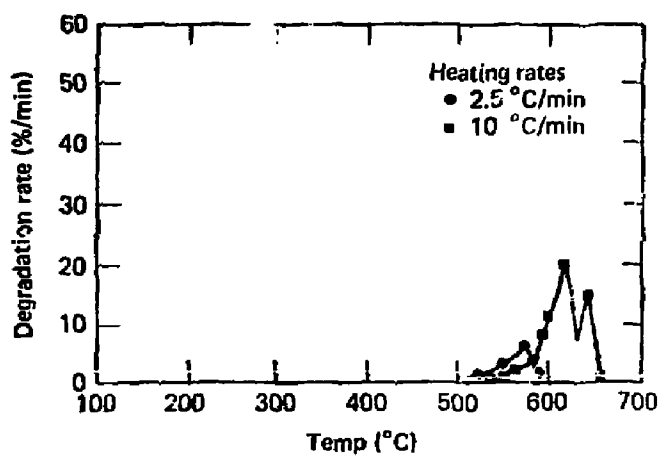


Fig. 14

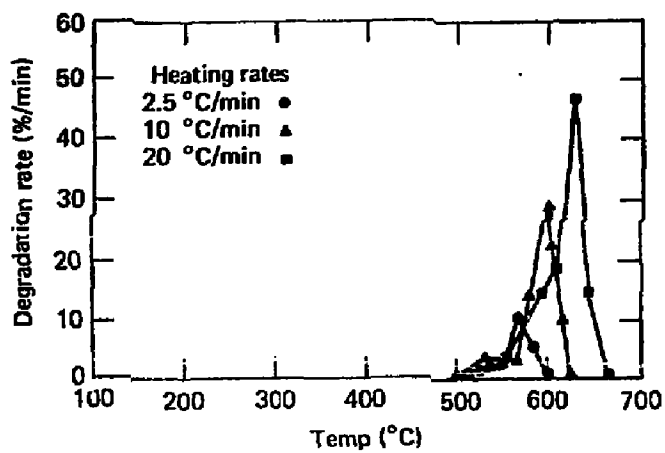


Fig. 15

unless thermocouples are embedded in the sample or shielded from the flames. However, one can determine the initial time from ignition at which the corrosive products are first seen.

3. Neoprene has the lowest decomposition temperature. We did not detect HCL as a degradation product because it was probably absorbed by CaCO_3 , an additive frequently included in neoprene formulations.
4. PVC has the next lowest decomposition temperature, generating HCL between 290 and 400°C. The effect of heating rates and air on the degradation rate of PVC is most pronounced in the dehydrochlorination region.
5. With the exception of polyethylene, air does not lower the initial decomposition temperatures of the insulations. The initial decomposition of polyethylene is lowered from 400°C in nitrogen to 230°C in air.
6. Of the four insulations studied, Teflon is the most stable at high temperatures since it does not start decomposing until 500°C.

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